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THE MODERN CALORIMETER

BY

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American Chemical Society
Monograph Series

BOOK DEPARTMENT

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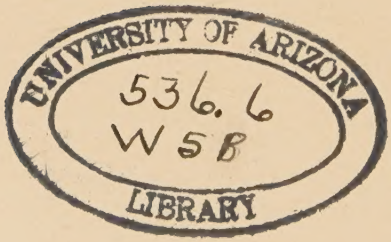

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

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The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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Preface

This book is, to an unusual degree, an experiment. Considerable portions of it are devoted to estimates and computations concerning the attainable precision or reliability of various methods or designs in calorimetry. These calculations are such as experimenters often make in planning their own work, but almost as often leave buried in their note-books. This book involves an attempt to show what may be the value of publishing such calculations in a systematic way, in order to benefit those who would ordinarily make only vague estimates and perhaps suffer seriously in consequence, and also in order to secure correction of the errors and partial views which even the best workers do not altogether avoid when working alone. To secure this end discussion and criticism seem almost essential; any single opinion or authority quite inadequate.

In accordance with this point of view the presentation differs from various specifications of procedure, to which it has some resemblance, in trying to deal more in demonstration and to be less *ex cathedra*. It has seemed best, however, to focus attention on such topics as my own experience has better fitted me to present.

Similar but briefer treatments of many of the topics here considered have already been published in articles from the Geophysical Laboratory, especially in 1918. The material of these, however, has been almost entirely rewritten, as well as expanded. All the experimental work of my own which is mentioned here was done as part of my regular work as a member of the Geophysical Laboratory staff.

This book owes much to the criticism and the suggestions of Arthur L. Day, and also of Theodore W. Richards, the late T. S. Sligh, Jr., Frederick Barry, and Robert B. Sosman.

WALTER P. WHITE.

Introduction

Among scientific subjects calorimetry has its full share of the interest that comes from ingenuity and invention. The equally important matter of studying the conditions of precision has not been as fully cultivated, with the natural consequence that comparatively ineffective use of the ingenious devices, tolerance of easily avoidable errors, and even striking disagreement on simple and fundamental matters are abundantly revealed in the literature.

In all subjects there has doubtless been a tendency to consider invention more fascinating and more deserving of admiration than investigation, but in calorimetry there is a special reason for the relative neglect of careful study. The calorimetric processes depend on temperature distributions and heat flows; things invisible, hard to measure or control with exactness, and unfamiliar to many of those whose scientific interests have led them into calorimetric work.

Of late these difficulties have been attacked, especially by Richards, Dickinson, and their collaborators, by Barry and by the present writer, so that calorimetric methods and our understanding of them have both been improved. The following pages aim to give a unified account of this recent progress, which reduces largely to the discussion of a single topic, the measurement of heat by means of temperature change in suitable bodies. Some important matters are passed over, partly because I have not had the same experience with them as with the topic discussed. Among these omitted portions of the recent progress are the flow method and various accessory manipulations, such as improved methods of mixing in thermochemistry, adequately described in the original papers.

W. P. W.

Notation

θ Calorimeter temperature.

Θ Temperature at beginning or end of a calorimetric period, calling for maximum precision of measurement, and used to get the temperature rise or rate.

$\Delta\Theta$ observed changes of the same.

φ thermal head, or temperature difference of calorimeter and calorimeter chamber.

u temperature of outlying shield, or of thermometer when different from that of the calorimeter.

C temperature of the calorimeter chamber.

η thermal leakage effect, expressed as a change in the calorimeter temperature.

$\Delta\Theta'$ $\Delta\Theta + \eta$, "corrected," that is, complete temperature change due to the heat that is measured.

t time, never temperature.

T interval of time.

T_B time of the most rapid portion of the temperature rise.

V rate of change of Θ, the calorimeter temperature.

V in Section 7, velocity of flow of water.

w "constant" rate of change of calorimeter temperature, i.e., part of the rate which is not dependent on φ, usually consistng mainly of the heat of stirring.

Q measured quantity of heat.

K thermal leakage modulus.

K_1 modulus of the shield with respect to the calorimeter.

K_2 " " " " " " " " chamber.

K_3 " " " calorimeter with respect to the shield.

K_4 " " " " " " " " chamber.

K_n a series of terms in K_1, K_2, etc.

K also thermal conductivity (in Section 9 and the last part of Section 20).

H heat capacity of calorimeter.

h heat capacity of shield.

h_1, h_2, u_1, u_2, K_1', K_2', etc., capacities, temperature, and leakage moduli of a series of shields.

K'' and K''', combinations of K_1', K_2', etc.

L lag, as a time, usually in minutes.

f fraction of heat capacity or surface affected by a lag.

S space, or gap thickness.

x as subscript, denotes the experimental period.

r " " " a rating period.

a " " " an anterior period.

θ_x, φ_x, θ_r, φ_r, θ_a, φ_a, average values of Θ or φ for the indicated period.

Θ_1, Θ_2, Θ_3, Θ_4, calorimeter temperatures at beginnings and ends of 3 possible periods. Θ_2 begins the experimental period; Θ_3 ends it.

ε various small errors.

R probable error.

R in Section 3, ratio of heat capacities of water jacket and calorimeter.

A allowable error, here arbitrarily taken as 3R, or about the error occurring once in 300 pairs of duplicated experiments.

A also the maximum ordinate of an exponential temperature-time curve.

A also an area.

τ a time characteristic of an exponential temperature-time curve.

A–C the jacket temperature (in Figs. 3 and 4).

B–C a line roughly equivalent to the curve of rapid temperature rise (Fig. 8, Sec. 8).

T_B the time of this rapid rise.

a, b, c, etc. temperatures during the rapid rise (Section 4).

a, b, c, etc. successive temperature readings during a rating period (Section 6, Equations 21, 22).

l in Section 7, length.

d " " " diameter of pipe.

P pressure.

n a numerical factor, sometimes proportional to linear dimensions.

In Sections 9 and 20, and in Equation 43, other notations taken from previous papers are left, unchanged, but are explained where they occur. The same is true of the lettering in Fig. 16, Section 24.

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THE MODERN CALORIMETER

Chapter I

Outline of the Subject

Any body into which the heat to be measured can be brought and whose consequent temperature change can be observed may serve as a calorimeter. The practical essentials of a calorimeter are provided by an open can of water, a thermometer, and a hand stirrer, the greatest advantage of the water being that it can be made, by stirring, to give a uniform and so a definitely measurable temperature. Crude apparatus of this sort, if the thermometer is adequate, will often give a precision of 1 per cent, for the total heat loss to the environment and the effects accompanying it can usually be made as small as this, and the main temperature change, a matter of simple thermometry, is the only other quantity to be measured during the experiment.

As greater precision is sought the requirements increase rather rapidly, so that the whole subject soon takes on a very different aspect. A determination of the thermal leakage, or quantity of heat lost from the calorimeter during the measurement, is the first step toward greater precision. If this is determinable within 20 per cent the total precision will be increased about fivefold, which is a liberal reward for the additional manipulation required. Still greater precision requires attention to the various conditions affecting the thermal leakage, such as room temperature, evaporation, or stirring, but an increase in thermometric precision also will be indispensable.

The Temperature Loss

There is a difference of opinion as to whether thermal leakage is necessarily the chief source of error in calorimetry, but it is undoubtedly responsible for most of the experimental features and devices in accurate work.

The value determined for the thermal leakage is often spoken of as a "correction," which subtly suggests that the leakage itself is some-

how wrong. It seems more profitable to consider that the heat measured by the calorimeter is measured in two ways. One portion of it remains in the calorimeter, where it produces, and is measured by, a simple change of temperature. The other portion of the heat ordinarily flows away according to known physical laws, whose application enables its amount to be determined like that of the other portion, tho a little less directly. Since this is actually determined in terms of temperature we have for the whole experiment a temperature rise, observed, and a temperature loss, calculated. The principle of the calculation is this: The leakage from the calorimeter depends on the thermal head, which is the effective difference of temperature between the calorimeter and its total environment; if the thermal head is observed during the experimental period (X-period), the heat loss can be calculated. The law which is nearly always used is that the leakage rate is proportional to the thermal head; or, if φ is thermal head and V the rate of temperature change in the calorimeter, then $V = K\varphi$, where K is the *thermal leakage modulus,* or thermal leakiness of the calorimeter. It is almost always considered worth while to modify the construction of the calorimeter, if necessary, so that φ may be accurately proportional to V, and the advantage of the above simple formula may be obtained. The value of K, the proportionality factor, can be measured at any time by observing rate and thermal head, V and φ, when no other source of temperature change than leakage is present. K is commonly thus measured in a *rating period* immediately after each X-period; this largely eliminates the effect of changes in K which are likely to occur from time to time. If care is taken to order the installation so that K is constant from day to day, rating periods can be dispensed with in daily work, giving short methods not of the highest precision.

Secondary Effects. The description up to this point is simpler than the reality, since it omits two things. In the first place, the heat produced by the stirring, which is appreciable in precision work, can not be treated by the formula $V = K\varphi$, because unlike the thermal leakage it is not proportional to the thermal head; second, in most installations it is impossible to read the thermal head directly, since the environing temperature is determined by a number of different bodies, more or less scattered thruout the room. Both of these difficulties have been surmounted by methods, to be described later, which demand that the environing temperature, if it is not known, shall at least be constant. In work of modern accuracy, however, this requirement of constancy practically demands temperature regulation, and

also a simple and uniform environment, such as a water jacket. And with this latter demand met, the question whether the environment is regulated or observed becomes of secondary importance.

The determination of the escaping heat thus depends, in the main, on few things; the temperatures of calorimeter and environment, and the constancy of the leakage modulus, K. The time for which the leakage must be determined is usually not over 10 minutes, and the amount of heat involved not more than 3 per cent of the whole. The necessary temperature control and measurement is therefore not difficult; the difficulty of knowing the rapidly changing temperature of the calorimeter surface is the only source of error which need vie with those in the measurement of the temperature rise.

Minor Effects. There are, however, a number of minor effects which, negligible ordinarily, imperatively demand consideration as the precision passes 1 per mille, or the time, an hour. These are to be discussed in detail; the best recognized are: (1) The heat produced by stirring; (2) the passage thru jacket walls of a heat flow from outside whose value cannot be found from the jacket temperature; (3) the unavoidable failure of stirring and conduction to give thruout the calorimeter a completely uniform temperature. This latter effect produces lags, that is, partial temperatures which are behind, or ahead of, the temperature of the measuring thermometer; these have had an important place in the developments of the last twenty years. (4) Larger than any of these is the effect of evaporation, which would cause the most serious errors of all were it not possible to deal with it by suppressing or suitably confining the evaporation. The means of doing this, though, are so inconvenient that there is a considerable tendency to avoid them at the risk of incurring the errors.

Experimental Arrangements

The experimental arrangements used to control these various effects naturally vary according to the precision sought. An open unprotected vessel, as has just been said, may be good for 1 per cent under favorable conditions. At the other extreme is the calorimeter shown in Figure 1, (1) closed completely against evaporation; (2) with a shielding mass of circulating water surrounding it completely; (3) with the stirring controlled so as to be constant; (4) with all projecting or accessory parts made to be as small and as near the calorimeter temperature as possible in order to avoid lags; (5) whose jacketing water may also be kept constant by a thermostat; (6) with which precautions have been taken against the flow of heat thru the protecting jacket

along stirrer rods, thermometers, or wires, by thermostating the room temperature, and by suitable choice of materials and design; and (7) having a *convection shield, S,* of very thin metal between the calorimeter and the inner water-jacket wall, in order to lessen three different errors at once, as will be explained further on.

For intermediate degrees of precision experimenters have shown a tendency to choose the easier features of a high precision installation,

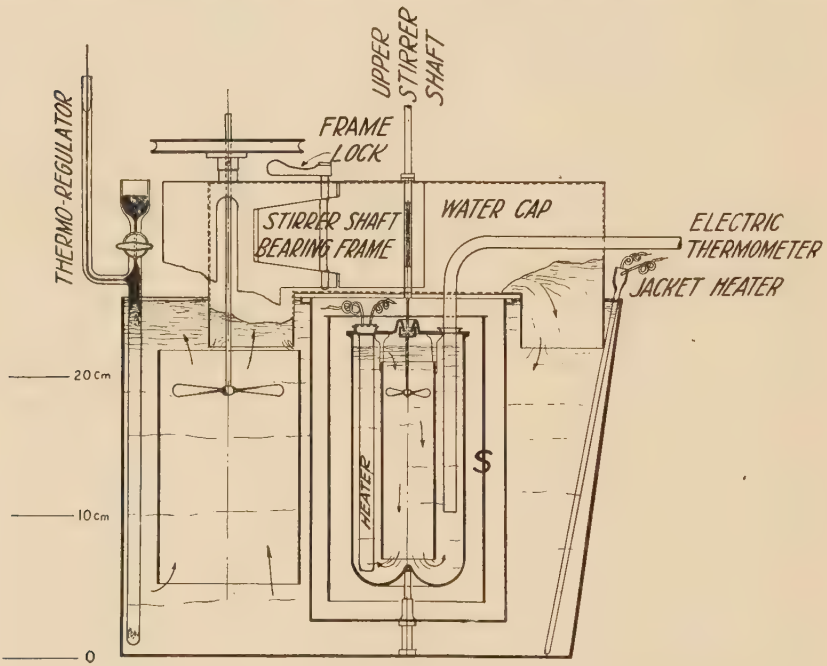

FIG. 1.—Highly-developed calorimeter, with complete shielding against evaporation and room temperature uncertainty; with thermostatic jacket temperature control and provision for rapid jacket heating; with convection shield, S, of gold-plated silver, 0.05 mm. thick, which permits using an air-gap 3 cm. thick, yet without convection error.

omitting the harder ones. A water jacket is nearly always put below and around the calorimeter, but the difficulty of bringing it above is avoided. The direct effect of room temperature is thus made about a fifth of what it would be with no protection at all.

The preceding description applies to what may be called the logical, or straightforward method of dealing with the thermal leakage. Numerous special devices also have been suggested for avoiding or facilitating this determination, and several of these have been recognized as having a permanent and standard value.

Ice Calorimeter

The ice calorimeter, which dates back to the very beginning of calorimetry, is the most successful of all devices in eliminating thermal leakage, since the heat transfer takes place in the interior of a mass of ice whose outer temperature, accurately zero, is the same as that of other ice which surrounds it.

Vacuum-walled Calorimeter

The vacuum-jacketed vessel was invented by Dewar [1] to serve as a calorimeter, and only long afterward became popular as a guardian of hot or cold refreshments. The vacuum diminishes directly the tendency toward thermal leakage, that is, the leakage modulus K, and hence, as might be supposed, may lessen the errors or difficulties that are due to leakage. This is an insufficient and possibly misleading account of the matter, however. To illustrate: The fundamental equation for the temperature loss is

$$\eta = VT = \varphi KT \qquad (1)$$

Here, where T is the length of the experimental period, K is a multiplier of the thermal head, φ, and therefore multiplies any error in φ; hence with K made smaller the effect of such error is lessened. But the *error* in φ is ordinarily negligible, hence, as far as it is concerned, the only gain from a diminished K, usually, is the ability to indulge in a *cruder treatment* of φ. The chief gain actually comes, as will be shown later, in indirect ways, as from the lessened effect of lags and from the possibility of stirring more slowly. The variation in K also tends to be smaller. The very serious adsorption error treated by Barry is eliminated by inclosing the sides of the calorimeter. The diminution in K which the vacuum-walled calorimeter brings is much less than is often supposed; at most four-fifths, and sometimes only one-half the value for an air-surrounded vessel. This, however, is often well worth while.

Adiabatic Method

A third scheme, the adiabatic method, consists simply in manipulating the jacket temperature so as to keep it always nearly equal to the calorimeter, thereby eliminating leakage. Here, in the equation $\eta = VT = \varphi KT$ it is φ which is diminished. The diminution of φ can evidently be made far more complete than the diminution of K

[1] Weinhold, however, preceded Dewar in the construction of vacuum-walled vessels. Person, 1851, made a vacuum-walled calorimeter, but lacked the technical knowledge to make it successful.

made by the vacuum-walled vessel. Nevertheless, since appreciable error in measuring φ is usually easy to avoid and since the error in adjusting the jacket temperature is greater than that in measuring φ, anyway, this method does not diminish, as it is often supposed to do, but actually aggravates most of the errors that come in dealing with φ. As with the vacuum vessel, its advantages are indirect. As the small value of K in that vessel eliminates the errors in φ, the small value of φ in the adiabatic method lessens errors from inconstancies in K which are far more serious, especially those due to evaporation and convection. Hence this method is generally regarded as indispensable in protracted experiments. It also renders possible, in a way to be explained later, a construction which diminishes thermal leakiness, and with that, error from lags and some other sources.

Joule's Twin Calorimeters

A fourth method due to Joule (1845) makes no attempt to diminish the thermal leakage, but eliminates its effect by matching or compensating it. Twin calorimeters are used, which are heated by the same amount. In Pfaundler's modification, the one most used, the principal thermometer reading is a direct differential thermoelectric reading between the two calorimeters. It is clear that even when the similar calorimeters are cooling rapidly this difference may be as stationary as the temperature in the adiabatic method. This advantage, however, can easily be overestimated, since in any apparatus thermal leakage error comes from irregularities, and a failure of similarity, sometimes unavoidable, will act as an irregularity in the twin method. The peculiar, and chief, advantage of the method is in reducing the determinations of temperature and of heat capacity to purely comparative measurements which can be accomplished by relatively simple differential apparatus. This was the advantage which Joule had chiefly in mind.

The Convection Shield

One valuable device consists simply of a partition of thin sheet metal in the middle of the air gap, parallel to the calorimeter surface, as in Figure 1. This device has long been used, but apparently until recently without much appreciation of its best form, which is as thin as is mechanically feasible, or of its chief function. This is its very marked tendency to lessen convection currents, which permits the air gap to be thickened, and the thermal leakiness accordingly reduced, with a diminution of important stirring and lag errors. This gain is about as great as that from the adiabatic method for short periods,

and a little less than that from the vacuum wall, but is secured very simply, with practically no effect on the manipulation needed when the shield is not used.

Aneroid Calorimeters

Another class of calorimeters, the aneroid, or fluidless, substitutes conduction for the circulation of a fluid as a means of securing temperature uniformity. These can be used at extreme temperatures; at ordinary temperatures they avoid the difficulties connected with evaporation and stirring. Lags are especially serious with them, on account of the more imperfect temperature equalization.

Heat Capacity Determination

In all the calorimeters just considered, except the special twin and ice calorimeters, the thing measured is change of temperature; the heat is the product of this change by the heat capacity of the calorimeter, according to the equation

$$Q = H(\Delta\Theta + \eta) = H\Delta\Theta' \qquad (2)$$

where H is heat capacity, $\Delta\Theta$ observed temperature rise, η temperature loss. A knowledge of the heat capacity is therefore of fundamental importance; an error in it may run, systematically, all thru a series of results, without giving any sign of its presence; several calorimetric schemes have had as a prime object the avoidance of such errors. The capacity can be calculated, well enough for cruder work, from the amounts and specific heats of the calorimetric materials. For precision this method is extremely unsatisfactory; it is better to measure some standard amount of heat, given electrically or chemically or in other ways. The calorimeter thus becomes a transfer instrument, and various systematic errors in the method used also tend to be canceled.

The Most Important Things

The more available of these special methods offer a rather moderate gain in precision, the lessening of certain particular errors by a factor less than 3. Moreover, in most cases hitherto these methods have not been carried out so as to secure even this moderate gain. Hence it is not surprising that as calorimetric precision has been increased the regular method has given as great precision as the special ones. Precision, as a rule, mainly depends on two things; first of all, accurate thermometry to measure the retained heat, and second, accurate knowl-

edge and control of the conditions which determine the leakage of the lost heat; and most of the methods do not differ greatly in respect to these fundamental requirements. For example, soon after its introduction Richards' adiabatic method was developed to a point where it yielded accurate results which marked a real advance in calorimetry. But effective operation of the adiabatic method demanded a thoro control of the environment. And when such control, plus an elimination of evaporation, was independently applied with more ordinary methods, the advance of the adiabatic method was fully paralleled for ordinary short experiments.

Chapter II

The Fundamental Processes and Measurements

Section I. Errors in General

The relation between individual errors and the precision of the experiment as a whole is fundamental in any discussion of either.

Measurements Outside the Calorimeter

Quantities of heat cannot be kept as individuals and measured from time to time, like weights or volumes. The heat evidently must be produced or otherwise furnished at the time it is measured, hence every calorimetric experiment is a determination of the relation between the heat and the bodies or processes which yield it, and the final accuracy depends just as much upon the precision of the measurements defining the source of the heat as upon those directly connected with the recipient of it. In most cases today, probably, the desirable calorimetric precision is less than might readily be attained, but is all that is worth while in view of errors elsewhere in the experiment, and improvement in the calorimeter then consists in making this precision easier rather than greater. Hence a knowledge of the conditions of precision in the calorimeter is important, in some cases to increase precision, but in others, to diminish manipulation safely.

Of the various quantities which enter the final calorimetric equation, one, of course, is unknown, and to be found by means of the others. Thus, in the method of mixtures, where the equation is $H\Delta\Theta' = MS\Delta\Theta''$, the object may be to find the heat capacity H of the calorimeter (that is, to calibrate) or the specific heat, S, of the body of mass M which yields heat on changing $\Delta\Theta''$ degrees, or the temperature, $\Delta\Theta''$, to which a known body is first heated. Which quantity is unknown, however, makes no difference to the calorimetric manipulation, since this always consists in the determination of the temperature rise and loss. Calorimetric procedures should be classified, therefore, with respect to the apparatus and methods, not with respect to the quantity whose value is to be found.

Control of Errors in the Calorimeter

In calorimetry, the mere multiplication of observations to diminish the error of the calorimeter can be shown to be very ineffective, with three exceptions. A moderate improvement in technique is generally a much easier way to reach the same result. The first exception concerns the single repetition, or duplication, of each experiment to guard against blunders or unnoticed accidents. This duplication, or some substitute for it, will probably be regarded as essential by the careful experimenter, unless he is almost superhumanly skilful. But this duplication is generally sufficient, except for isolated experiments, where the occasional coincidence of two similar accidental errors may well be guarded against. If, out of a series of determinations made in duplicate, most of the pairs agree, the absence of extraordinary *accidental* error in all of these seems beyond reasonable doubt. Every pair which shows agreement increases the confidence felt in the others.

The general futility of much repetition can be seen by considering the different classes of errors.

Systematic Errors and Repetition of Observations. Systematic errors, by their very definition, are not remediable thru repetition. In fact, with them the only hope from repetition lies in the chance that it will prove not to be repetition at all—that some unintended variation may perhaps neutralize or at any rate reveal the systematic error. Fortunately, this uncertain and indefinite chance is not needed if the calorimeter is made a transfer instrument, as it should usually be in accurate work. The elimination of systematic error may then even extend to the associated measurements, as is discussed more in detail on page 132.

There are, however, two classes of *partly* systematic error whose discussion demands special attention.

Errors Varying Systematically with the Material or the Kind of Observation. Errors systematic with and varying with the different bodies experimented upon or with different temperatures or other conditions of observation may arise in ways like the following:

(1) Bodies may require different times to reach equilibrium in the calorimeter, and the difference in time may cause a difference in the determination of the temperature loss; (2) Bodies may raise the calorimeter temperature by different amounts, with a similar result; (3) Where different liquids are used in the calorimeter, stirring heat, temperature equalization, and evaporation are likely to vary. These errors, like those completely systematic, evidently are not lessened by

strict repetition. Variations of conditions, accidentally accompanying the repetitions or introduced on purpose, may possibly reveal such errors, but will give an imperfect elimination of them, much less perfect than repetition gives of accidental errors. A more effectual way to deal with this class of partially systematic errors, and one which this book tends to show is really easier, is by design or method to eliminate liability to them. This involves attention to stirring, to evaporation, and to heat losses generally. A similar conclusion can be drawn regarding errors in the associated measurements which are systematic with different substances or temperatures.

I have just said that even variations in apparatus and method eliminate this class of errors only imperfectly. There are two reasons for this. (1) The proper analog to, say, ten repetitions of an experiment to eliminate a purely accidental error would be ten different calorimeters, or at least ten different procedures, to eliminate systematic error. To provide these is usually a prohibitive labor. (2) The errors of the different calorimeters would not be nearly as well distributed about zero as purely accidental errors are. For instance, if the differing volatility of various liquids caused partially systematic errors these would be eliminated by the use of different calorimeters only if these calorimeters were so chosen or adjusted that evaporation caused positive errors in some and negative in others. And this adjustment could hardly be made unless the experimenter not only recognized evaporation as a source of his "concealed" systematic errors, but knew a good deal about the peculiarities of his calorimeters with respect to it. And if he knew all that, he could diminish the errors more effectively than by more or less random variation of apparatus.

Undoubtedly the theoretical "probable error" is lessened even by random variations. But this probable error is, practically, a different thing in different cases. For instance, the mean of a series of photometer comparisons is a close approach to a definite physical fact. But if Mr. A knows only that half the passengers were saved on a shipwrecked vessel carrying a friend the "probability" that his friend is alive, namely, one-half, corresponds only to the actuarial value of his hope, since the friend is really either completely safe or completely drowned. And similarly, while the combining of different observations gives a result almost certainly more accurate than most of them individually as far as accidental errors are concerned, the combining of different methods or calorimeters may or may not lessen errors systematic with anything which is not varied. This is because the combining of errors of opposite signs, which is the chief source of

the gain with accidental errors, occurs in the other case only as a fortunate chance, like the possible rescue of A's friend. This chance may seem to justify the variation of apparatus in any given case, but the elimination of error by any sort of random repetition is less perfect where the error is systematic. And this is all I undertook to prove.

There are certain systematic differences likely to exist between the calibration of a calorimeter and its other work which can be anticipated, and investigated by experiments varied in very definite ways. Some of these are treated on page 36.

Errors Systematic with Time or Weather. Change of room temperature or humidity, and all sorts of changes in the apparatus, such as deterioration or fouling of heat-radiating surfaces, loosening of stirrer belt, development of unintended friction, or deterioration in the fit of covers, may change the effective heat capacity of the calorimeter. If different bodies are experimented on at different times the errors caused by these changes may become irregularly systematic with the different bodies altho the bodies themselves are not at all responsible. The same applies to experiments on the same body at different temperatures, or under otherwise different conditions.

Mere repetition may be a very wasteful way to deal with such errors, but suitable repetition may do much to reveal them. This is the second case where repetition cannot always be said to be very ineffective. For changes due to weather, experiments need to be repeated in different weathers; for deteriorations and other changes that do not reverse themselves, any experiment, as the calibration, may be repeated after a sufficient interval. The most effective repetition thus requires a knowledge of the probable sources of error. Indeed, no other class of errors affecting the calorimeter offers any better opportunity for the experimenter's knowledge and acumen. But knowledge and acumen evidently are apt to be more effective in preventing the errors which judicious repetition often can only detect. Nevertheless, an occasional check of the constancy of the calorimeter thru the repetition of some suitable experiment seems a desirable practice and the regular duplications may be done at considerable intervals, where this is convenient, on the chance that unsuspected variations may sometimes be revealed. But extensive repetitions as a means of avoiding error from change of conditions are again likely to be more laborious and less effective than the adoption of suitable methods and apparatus. The proof offered for this will come thru the detailed discussion of methods.

Changes in the apparatus which do reverse themselves are apt to

be systematic in respect to determinations immediately repeated; accidental for those repeated at considerable intervals. But even in the latter case repetition gives not so much a remedy as a warning, and a rather unsatisfactory one at that.

Repetition to Detect Errors. Repetition with a view to detecting errors is generally best accomplished by proceeding so as to exaggerate the errors. Indeed, this is the only practicable way if the errors are small. Such repetition clearly is a very different thing from repeating in order to decrease the error of the experiment repeated. It is to be classed as experimental study of the calorimeter. As such, tho often very important, it is also decidedly laborious; hence it is often well to avoid this kind of repetition also by employing superior technique.

Errors from the Personal Equation. In so far as the peculiarities of the observer affect the results of calorimetric experiment these should be taken care of in the calibration. Where several workers coöperatete the determinations made by one of them may not correspond with those made by another. The possible resulting partially systematic error may be detected or corrected by having the two duplicate experiments done by different observers in some or all cases.

It is a familiar experience that observers get less concordant results at first, or when they have got out of practice, and some systematic error seems likely to go along with the accidental. The repetition which is desirable to overcome this difficulty should not be confused with repetition regularly used to lessen normal accidental error, which, as will be shown immediately, is of much less value. It may be classed, tho, as a third kind of desirable repetition.

Accidental Errors and the Ineffectiveness of Repeating Determinations. The great importance of once repeating each experiment as an insurance against blunders and accidents has been mentioned, and probably needs no exposition. Duplication also reduces the probable accidental error to $\sqrt{2}$, or 0.7 of its value for a single determination. But the repetitions become rapidly less effective as their number is increased. Two more only brings the probable error to one-half, with an average effectiveness for each only one-third of that for the first repetition. If the probable accidental error of a pair of experiments is to be made a third as great by repetitions, $3^2 \times 2$, or 18 experiments must be carried out, or 16 additional ones. It is rather rare to find experiments as elaborate as the calorimetric repeated as many times as that. On the other hand, it will appear later that an equal diminution of most errors accomplished thru suppression of evaporation, control of stirring speed, and in similar ways, is usually much less of

a burden. In some cases there may be doubt, but the presumption seems to be against much reliance on repetition after the first duplication. The presumption is weakest where only a few determinations are to be made with the apparatus, or where the improvement needed is replacing the mercury thermometer by a relatively elaborate electric system.

Detection of Particular Errors by Duplication. It is more important to be assured that large errors are absent than to have very small values for the small ones. Duplication seems often to be supposed to be of use in detecting large errors. Thus, when duplicates differ by less than the allowable error they are taken as satisfactory; when they differ by more than that, further repetitions of the experiment are undertaken. Such a procedure when large errors from accidents and blunders are concerned carries out the chief purpose of the duplication, but is almost useless with accidental errors—that is, errors distributed according to the Probability Law.

The reasons for this are as follows: The errors to be eliminated are in the average of two determinations; the warning is given by the discrepancy between the two. In order that any good may be accomplished the two things, error-of-the-average, and discrepancy, must be large together. But this happens only when a rather large error is combined with a small one. Errors of opposite sign tend to have very small algebraic sums, so that the large discrepancies which they are apt to show are false alarms. Errors, both moderately large, of like sign combine to give equally large averages, but present no discrepancies large enough to give warning of these. And the moderate-sized errors are so much more numerous in a probability curve than the large ones, that the concealed final errors far outweigh the errors which both deserve and get attention. So, also, do the false alarms. This is illustrated with the aid of Figure 2, which is simply the ordinary probability curve, with abscissa proportional to the magnitude of error, and the various areas showing the number of errors of each size which occur in 2000 observations, that is, in 1000 pairs. R is the magnitude of the probable error, or error such that half the number are larger than it.

Now suppose, for instance, that each pair of duplicate determinations differing by $4R$ is to be marked for further repetition. These pairs will give the maximum final error only when a single error of $4R$ or more combines with an error of R or less; the final error thus marked for correction will be about $2R$; and evidently less than half of the 14 single errors exceeding $4R$ will be concerned. But of the 72

errors between $3R$ and $4R$ in magnitude, over one-fourth, combining with those of the 900 errors between R and $3R$ which have the same sign, will give final errors of $2R$ or over, yet with small discrepancies. In fact, less than one-twentieth of the errors-of-the-average larger than $2R$ will be revealed by discrepancies greater than $4R$; for smaller discrepancies than $4R$ the proportion revealed is larger, but for every error detected, at least 5 others as large usually escape. In actual experiment the proportion of rather large errors is usually greater than the theoretical, but a better insurance against accidental errors, of a certain magnitude, in the averages of pairs of results will clearly be to make the probable error, R, small enough, say one-third of that magnitude, and then take the best possible care to avoid accidents or blunders.

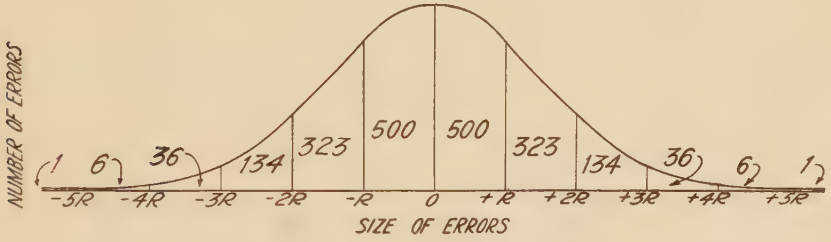

FIG. 2.—Diagram; probability curve.

Adjusting the Value of the Probable Error. The control of the probable error of the calorimeter is therefore a very important feature of the effort to secure sufficient and not extravagant precision. It is so not only for the reason just given, namely, that it is the only tolerable way to avoid large accidental errors, but also because the accidental errors are the ones of paramount importance in the calorimeter itself, given proper modern procedure. The practice of experimental calibration eliminates strictly systematic errors; and the partially systematic errors mentioned in the pages just preceding are evidently such as disappear almost entirely when the causes of accidental error are suitably lessened.

While the probable error defines the precision of the calorimeter as well as anything can, it does not indicate directly the value of the results. Errors larger than the "probable," and some considerably larger, are probably present, and the confidence one can feel in the results is measured rather by the error which is known to be pretty certainly absent. In this book, therefore, precision is usually specified by means of a final error so rare as to be practically negligible, namely,

one occurring, probably, once in the averages of 300 pairs of duplicates. Since the size and the rarity of errors increase together, this error is larger than the "probable," and is, as can easily be shown, equal to $3R$, or 3 times the probable error. The choice of $3R$ is of course arbitrary, and purely a matter of convenience. A precision of, for instance, 1 per mille as measured by the probable error, is only 3 per mille as measured by the negligible rare error $3R$, and either of these facts involves the other. An experimenter will often consider that he can tolerate, or allow, an error of a certain magnitude and no more. In that case it clearly would not do to let the probable accidental error, R, be as large as the "allowable error." But the probable error might well be as large as one-third of the allowable, making the allowable error $3R$, and therefore rare, and that is what will be assumed in this book. Of course any experimenter may choose some other value than the arbitrary $3R$, if he wishes. The allowable error, the "assured" precision, and 3 times the probable error of a single experiment, then, are all three identical in the following pages. In the form of an equation—

$$A = 3R. \tag{3}$$

In designing or adjusting to get a desired value of the probable error: (1) The probable errors of the individual measurements may be supposed to be combined by the usual rule to get the probable error of their sum (R of the whole experiment), that is, to be squared and added, and the square root of the sum then taken. (2) This rule makes the effect of errors diminish very rapidly with their size. An error one-third of another will add only one-ninth as much to the final probable error. Errors only one-third of the larger ones may therefore be considered negligible, unless more numerous. (3) A very important qualification is that the prior assignment of values to errors is uncertain, and where the total number is not large the mathematical theory is not supposed to hold at all exactly. Hence an attempt should be made to have the errors less than theory demands, wherever this can be done easily. (4) It will be shown in Section 6, on the accurate temperature measurements, that these measurements, the largest source of error in most well ordered calorimeters (see page 62), are ordinarily equivalent in the total error to six single, independent observations. The accidental error of each one, therefore, should be, if A is the allowable final error of a pair of experiments, equal to $A \div 3 \div \sqrt{6}$, or $A/7.35$.* If this *allowable single error* is reduced to about

* The probable error is $A \div 3$, and this probable error is $\sqrt{6}$ times one of the 6 important single errors.

one-half, in order to provide the factor of safety just now said to be desirable, we have, say, $0.075A$, or $A/13$. If 2 other accidental errors of the same size are added the total probable error will be increased only in the ratio $\sqrt{8}$: $\sqrt{6}$, or by 15 per cent. This increase is much less than the uncertainty of any such reckoning as the present one. Hence if 2 or 3 other errors reach a magnitude, say, for simplicity, of $0.1A$ or of a single accidental thermometric error, the precision of the final result will not be compromised. This magnitude, $0.1A$, then, will be taken as allowable for each one of a few errors, tho a smaller value is always desirable.

$$\text{Single allowable error} = 0.1A \qquad (4)$$

Adjusting for Partly Systematic Errors. The reckoning just presented seems a fairly simple consequence of the elementary laws of chance, and, as such, applicable beyond reasonable doubt to all the errors that are typically accidental. But it does not apply so evidently to errors that are partly systematic. These errors, as has been shown, are all which may be influenced by such things as weather, furnace temperature, and amount and various characteristics of the materials experimented upon, and include the errors due to evaporation, convection, and jacket temperature uncertainty—that is, the most serious ones outside of the thermometric. Errors of these sorts, tho they may vary, will, under any given conditions, be biased always in the same direction. Nevertheless, each of these errors may be allowed to be nearly as large as 0.1 of the final allowable. The reason for this is as follows: If the probable value of any one of these errors is ε, then values of 5ε or 6ε will be rare. If ε is only 0.1 of the allowable, then the larger and rare error 6ε will still not exceed the allowable. The difficulty comes only thru the coincidence of such an error with others. But this coincidence will be a matter of chance, hence the above reckoning, and Equation 3, may still be used almost as well as for purely accidental errors. It cannot be used quite as well because in a pair of duplicates any particular accidental error is very unlikely to be repeated, whereas a partly systematic error is almost sure to be. Hence it seems desirable to keep possible systematic errors somewhat smaller than is considered necessary for accidental ones.

The two chief sources of partly systematic error appear to be convection and evaporation. Convection error, as will appear later, is due to change in the duration or the amount of the temperature rise, and is therefore always partly systematic, never largely accidental. It is an effect following fairly well known laws, whose magnitude can

be approximately estimated. When, therefore, a convection effect is $0.1A$ (0.1 times the allowable error), this is not a "probable error," likely often to be considerably exceeded, but a nearly constant and maximum value for the error, a much less formidable thing. A convection error as large as $0.3A$, even, would not be inconsistent with a final assured precision of $1A$; one of $0.1A$ seems sufficiently small.

Evaporation, on the other hand, is very uncertain. It is hard to know how much error it causes in any given series of experiments, still harder to know how much it might cause under different conditions. Hence, in spite of the good work that has been done with open calorimeters, some experimenters feel that the greater safety gained by prohibiting evaporation is well worth the trouble it causes.

Résumé of the Preceding Discussion. Of the discussion of errors up to this point some parts may be unfamiliar to many readers, and for this reason may be more likely to appear complicated or vague. It may therefore be worth while to restate briefly: An error, from its very nature, is an uncertain thing; as soon as it is definitely known is ceases to be an error. Some estimate of the errors, however, is desirable or necessary in planning calorimetric apparatus or work. The most vital part of such planning is estimating the different single errors. It is here suggested that the best way to pass from these to the error of the experiment as a whole is by dealing with the probable error in each case. The further suggestions that a factor of safety of about 2 be allowed, and that the error be finally stated, not as the probable error, but as a multiple of that, which shows directly the value of the result, are not essential. The position, strongly held by many experimenters, that mere repetition of experiments is a very inefficient way to lessen final error, will, I believe, be found true for the calorimeter as the other methods of improving precision are considered in detail. There are some cases, however, where repetition is advisable. Repeating each experiment once is much less inefficient than further repetition, and may reveal large unusual errors. It is illusory, however, as a means of revealing the normal larger accidental errors. Repetition is especially ineffective, and often is quite useless, in dealing with partly systematic errors.

Testing Precision. Analysis of the sources of error is at least comparable in value with experience as a guide to progress, for the experience obtained under one set of conditions may, alone by itself, be misleading as to others. But an experimental test of the performance of any calorimeter is usually highly desirable as a check on the estimates. In the majority of cases such checks *on the calorimeter*

cannot be adequately made in regular work, because the errors in the associated measurements preponderate. In these cases checks on the calorimeter are evidently of minor importance, as far as the work immediately in hand is concerned. Knowledge regarding the calorimeter itself, however, still may have considerable value. It can be obtained whenever the associated measurements are especially accurate, as they should be in calibration work. There seems to be no question that the calorimeter performance is best reckoned from such experiments by finding the probable error. Of course this applies to accidental errors, and these, as already shown, are the only ones that can be found by mere repetition. The discovery of partly systematic errors calls for special planning and may test the experimenter's knowledge and ingenuity. The same may be said of the possibility that the accidental errors of the calorimeter may vary as the associated manipulation changes. Some definite suggestions as to the testing for partially systematic errors in electric calibration are given below, page 36. In ways closely similar to these, other variations, for instance of the amount or time of the temperature rise, of the completeness of the control of evaporation, if this is not absolute, of the mean temperature of the experiment, can be made.

Utilization of Duplications. It has been said that to repeat each experiment once lessens to some extent the probable final accidental error, is futile as a means of detecting for correction any large accidental errors, but is valuable in detecting large errors due to blunders or unusual accidents. This latter use of the duplications implies that the blunders and accidents do not follow the Probability Law in having small errors much more numerous than large ones. A possible way to make this use practically is to take $5R$ or $6R$ as the criterion for a successful pair of determinations, making further repetitions when the discrepancy exceeds this value. If R, the probable error, has not yet been determined, $1.6A$ or 2 times A, the allowable error, may provisionally be used. Making the criterion as large as $5R$ or $6R$ insures that there will be very few experiments needlessly repeated on account of the coincidence of two rather large normal accidental errors with opposite signs, but also that extraordinary errors capable of producing a final error larger than $3R$ will mostly be detected and eliminated.

Variation of the Probable Error. One matter briefly referred to a few pages back deserves a fuller emphasis, because, altho really evident enough, it is seemingly very often overlooked. The precision of any installation depends on the conditions under which it is operated. The precision may vary from time to time, and is very likely

to vary from one laboratory to another. Experience alone is a rather poor indication of future performance. It establishes a certain presumption, but nothing more. Of course an exceedingly wide and varied experience will show the true value of apparatus or method, but as a rule an analysis of the sources of error seems quite as valuable as the record of experience.

Calibration and Accuracy

The two chief advantages of an experimental calibration have already been mentioned: (1) It is generally more accurate than a calculated calibration; (2) It largely eliminates the systematic errors of the calorimeter. Two classes of errors may pertain to such a calibration: (1) The associated measurement, that is, the standard of heat, may be in error; (2) Partial systematic errors may come in passing from the calibration to experiments of a different character. The accidental errors characterize all the work, anyway, and can here be diminished by repetitions of the experiment, less objectionable in the calibration, since that is done once for all. (1) Inaccuracy in the comparison standard of heat can be made negligible if the heat is produced electrically. (*See* Section 20.) (2) Differences in the character of the experiment may cause some errors to have an average value which is different in the calibration from that in the other work. Such differences are especially likely to occur when the calibration is electric, and in two ways. (*a*) The heating, if electric, may have to last longer than the other kind. This does not affect lag errors, but increases the convection effect (Section 8). A remedy lies in a careful treatment of the convection effect, also in exaggerating and thus roughly determining the error by varying the time of heating. (*b*) The electric heat may be produced in a different part of the calorimeter from that where the other heat is given to the water. This might cause error thru difference in the stirring lag effect (pages 65 *et seq.*). The error can be investigated by stirring very slowly, which exaggerates it, or by changing the position of the heater; but is probably better treated by the methods given in Section 7.

The danger of changes in the calorimeter after calibration, and the remedy, occasional repetition of the calibration or of some other suitable experiment which can be used as standard, have been mentioned.

Allowable Systematic Errors. In very many cases it is more important to know the differences or ratios of heat quantities than

their absolute values, and then small systematic errors can be neglected. Absolute accuracy may actually be needed more in otherwise crude commercial work, where each result is important in itself, than in many researches where considerably higher precision is demanded. In fuel testing this need has been met by the introduction of the practice of calibrating by the combustion of standard materials.

Proportional Accuracy and Delicacy of Measurement

Most errors can conveniently be grouped in two classes: The first have about the same value, whatever the magnitude of the quantity measured; these set the limit in delicate measurements, but can be made of diminishing importance as the quantity measured increases. In calorimetry, characteristic examples of this class are thermometric errors and those directly dependent on the room temperature and its changes. Errors of the other class are about proportional to the quantity measured, and preponderate over the first class more and more as they increase with increasing magnitude of this quantity, but are quite overshadowed by the others in delicate observations, where their absolute magnitude is small. Errors in heat capacity, lag effects, and defects in temperature distribution are examples of this second class. These errors are apt to be systematic. They are the ones which are lessened by experimental calibration.

Section 2. The Temperature Loss Formula

As soon as the addition of heat raises the temperature of a calorimeter, "thermal leakage," that is, the escape of heat to the surroundings, usually begins. The determination of this escaping heat is an essential part of the experiment. Since this determination is most conveniently made as that of the temperature change produced by the loss of heat, there are two temperature changes to be found; the temperature *rise,* symbol $\Delta\Theta$, due to the heat that stays in the calorimeter, and the temperature *loss,* symbol η, due to the lost heat. The sum of the two $\Delta\Theta + \eta, = \Delta\Theta'$, is the temperature change corresponding to the total measured quantity of heat.

The formula for determining the temperature loss is one of those details of method which any competent experimenter may expect to devise for himself as a matter of course. The simple procedures, however, are the most likely to suffer from lack of examination, and the best methods are seldom as evident as the fairly good ones. This formula, therefore, merits attention.

THE ASSUMPTIONS

It has already been said that the "cooling" of the calorimeter, that is, all change not due directly to the measured heat, has the formula $w + K\varphi$, where w is the heat of stirring, φ the thermal head,[1] K the thermal leakiness of the calorimeter. This statement is not rigorous; other very small effects are present, and neither w nor K is quite constant. Nevertheless, it is convenient to think of the spontaneous change as due simply to leakage and stirring heat, while for the mathematical

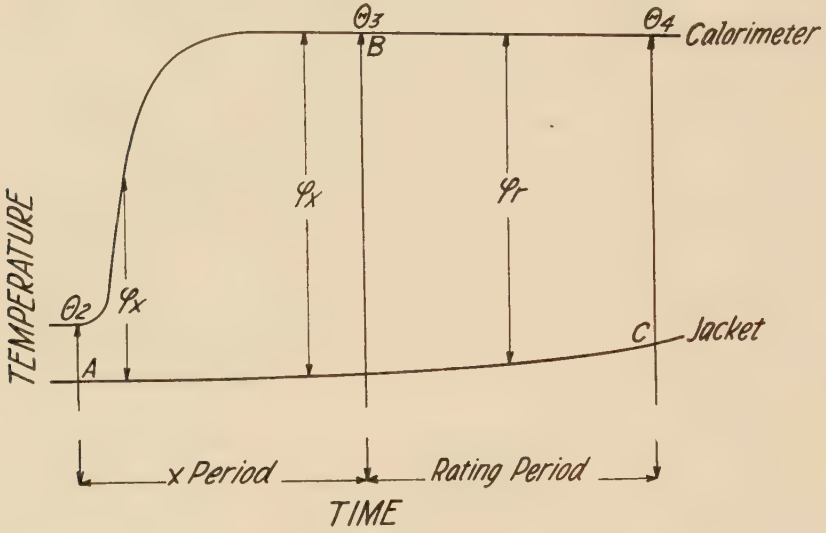

FIG. 3.—Temperature pattern of a typical calorimeter experiment. φ, thermal head; θ, calorimeter temperature.

calculation it is usually quite sufficient to treat that change as equal to $w + K\varphi$, where w and K are merely constants to be determined during the experiment. The practice of so determining them implies that they are (1) constant during the experiment, (2) not constant from day to day, otherwise there would be no need of determining them each time. Sometimes one or the other of these implications is not justified. Then it will either be necessary to take unusual precautions or be permissible to omit determining K or w each time.

Number of Periods. To find the two quantities, K and w, two equations, and therefore two differing rating periods, are needed, tho

[1] The height of water which produces a flow is known as the "head." By analogy with this, the difference of temperature between one body and another which causes heat to flow between them has been called "thermal head," denoted here by the symbol φ. So many temperature differences are involved in calorimetry that it seems needlessly confusing to denote them all by one name and symbol, since a retinue of qualifying adjectives or of subscripts would then be needed.

the solutions of the two are combined in a single formula. If one of these quantities is known a single rating period suffices, and this covers the very important case where the experiment is so conducted that the quantity is multiplied in the formula by a very small factor, since it then can usually be treated as known. A familiar case of this is making φ, the thermal head, about equal to zero, as in Richards' adiabatic method, when a determination of K is rarely needed, tho a period is still generally required for w.

The Temperatures During an Experiment.—The temperature pattern of an ordinary experiment and the observations needed are shown in Figure 3.

The jacket temperature is shown varying as a reminder that it may vary, tho its constancy is necessary for the usual temperature loss method. The difference of the temperatures Θ_3 and Θ_2 is the temperature rise. The difference $(\Theta_3 - \Theta_4)$ divided by T_r gives the rate, V_r. A series of observations during the x-period is used to get the mean temperature or thermal head, and similarly for the rating period, tho two observations are usually enough for that. All these observations are taken at definite times.

It is clear in the figure that φ_x, represented by the area AB, is nearly equal to φ_r, represented by BC. This approximate equality is advantageous, and characterizes most calorimetric experiments unless means are taken to prevent it.

The First Geophysical Laboratory Method

When the heat of stirring, w, is known, the formula is very simply derived.[2] Then V_r, the actually observed rate of cooling, less w, or $V_r - w$, is $K\varphi$, the rate proportional to φ. Therefore:

$$\frac{V_r - w}{\varphi_r} = K \tag{5}$$

and $\frac{V_r - w}{\varphi_r} \times \varphi_x$ is the proportional part of the rate for the experimental period, $w + (V_r - w)\frac{\varphi_x}{\varphi_r}$ is the total rate for that period, and

$$\left[(w + (V_r - w)\frac{\varphi_x}{\varphi_r}\right] T_x \tag{6}$$

is the formula for the temperature loss.

For the usual cases where $\varphi_x = \varphi_r$, nearly, Formula 6 can advantageously be altered. By substituting for $\frac{\varphi_x}{\varphi_r}$ the identically equal

[2] White, Walter P., *Phys. Rev.*, **31**, 547 (1910).

$1 + \frac{\varphi_x - \varphi_r}{\varphi_r}$, the formula is readily converted into:

$$\left[(V_r + (V_r - w) \frac{\varphi_x - \varphi_r}{\varphi_r} \right] T_x \qquad (7)$$

The advantage of (7) over (6) is that the multiplier of $V_r - w$ is a much smaller number, hence the multiplication is easier.

The form of (7) also makes it clear that w is really multiplied by a small number whenever φ_x and φ_r are nearly equal. This is true whether the formula is arranged to show it readily or not. Hence the Geophysical Laboratory method, tho it logically requires a knowledge of w, usually requires only the crudest sort of knowledge. When φ_x unavoidably differs considerably from φ_r, as in electric calibration, the method loses this particular advantage, tho it still retains its simplicity.

To get the formula in practical working form the original observations may be inserted. This gives:

$$\left[\frac{\Theta_3 - \Theta_4}{T_r} + \left(\frac{\Theta_3 - \Theta_4}{T_r} - w \right) \frac{\varphi_x - \varphi_r}{\varphi_r} \right] T_x \qquad (8)$$

If the periods are of equal length they cancel out of the formula. Then wT appears instead of w. If the periods are not equal, an equivalent form

$$\Theta_3 - \Theta_4 + (\Theta_3 - \Theta_4 - wT_r) \frac{\varphi_x T_x - \varphi_r T_r}{\varphi_r T_r} + w(T_x - T_r) \qquad (9)$$

is more convenient, since it is as easy to find $\varphi_x T_x$ and $\varphi_r T_r$, the integrals of the period observations, as to find the mean values. It is interesting, tho not likely to be often important, that by suitably choosing the lengths of the periods the fractional multiplier in (9) can be made nearly zero even when φ_x and φ_r are far from equal. The total multiplier of w, however, is the same in all these equivalent formulas, and depends on the relation between φ_x and φ_r.

The Regnault-Pfaundler Method

The first Geophysical Laboratory method, just described, in spite of its precision and simplicity, is comparatively recent and has been little used. There are two reasons for this: (1) φ, the effective thermal head, cannot be measured unless the whole environing temperature can be measured, and this is practically impossible with the incomplete jacketing commonly used elsewhere; (2) w, the rate independent of φ, can seldom be considered constant from day to day if evaporation contributes much to it, as it does in many installations.

Hence some form of the Regnault-Pfaundler [3] method has nearly always been used, in which the combined effect of w and the environing temperature at the time of the particular experiment is arrived at from measurements on the calorimeter alone. This solution for two unknown quantities naturally calls for two rating periods.

Very elaborate explanations of the Regnault-Pfaundler formula have been given, but a brief derivation closely analogous to that of (6) is possible. When the environmental temperature is unknown, the thermal head, φ, is also unknown, and the proportionality between φ and the rate V cannot be used directly. But that proportionality involves a proportionality between differences in φ and differences in V, and differences in φ are the same as differences in mean temperature θ, if the environing temperature is constant. Hence we may write:

$$K = \frac{V_r - V_a}{\varphi_r - \varphi_a} = \frac{V_r - V_a}{\theta_r - \theta_a} \tag{10}$$

But (10), tho obtained by slightly different reasoning, is identical in form with (5), with V_a taking the place of w, the constant rate, and difference of calorimeter temperatures corresponding to φ. Hence we may write, as in (6):

$$\eta = \left[V_a + \frac{V_r - V_a}{\theta_r - \theta_a} (\theta_x - \theta_a) \right] T_x \tag{11}$$

Putting in the actual observations this becomes, for equal periods:

$$\eta = \Theta_1 - \Theta_2 + \frac{\Theta_3 - \Theta_4 - \Theta_1 + \Theta_2}{\theta_r - \theta_a} (\theta_x - \theta_a) \tag{12}$$

which is the Regnault-Pfaundler formula in a simple form.

Improved Form of the Regnault-Pfaundler Formula. In view of the close analogy between the two formulas, (6) and (11), it is not surprising that this formula can be modified as the other was to give (7), with the more complicated multiplier much smaller in cases where θ_x nearly equals θ_r. The result, however, as can be shown by a transformation too complicated and too nearly evident to be profitably given here, is precisely that obtained by interchanging the two rating periods, a and r, of (11) to give

$$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a} (\theta_x - \theta_r) \right] T_x \tag{13}$$

This form, first given in 1911,[4] gives an easier multiplication whenever θ_r is nearly equal to θ_x, that is, in most cases. Since it is never any less convenient it ought to supersede (11).

[3] Pfaundler, L., *Pogg. Ann.* **129**, 117 (1866).
[4] White, Walter P., *Met. Chem. Eng.*, **9**, 451 (1911).

The Second Geophysical Laboratory Formula

An easier multiplication is not the only advantage of Formula 13. The greater ease comes simply from the small value of the factor $\theta_x - \theta_r$. But this small multiplier, when it occurs, means a diminution in the effect of errors occurring in the fraction $\frac{V_r - V_a}{\theta_r - \theta_a}$. And this fraction is an expression for the leakage modulus, K. Hence if a predetermined value of K is substituted for the fraction its errors also will be diminished by the multiplication. Such a substitution, therefore, can often be made, avoiding the need for the anterior rating period, and giving as a formula [5]

$$\eta = [V_r + K(\theta_x - \theta_r)]T_x \qquad (14)$$

This formula will, in fact, be permissible in the most refined work when conditions are reasonably favorable. Thus, it is possible to know K to 2 per cent at least, how much better is at present uncertain; the difference $\theta_x - \theta_r$ is often as small as $0.01\Delta\Theta$,[6] where $\Delta\Theta$ is the temperature rise. Supposing that it is $0.05\Delta\Theta$, and that KT_x has the rather large value 0.03, known to 2 per cent, the error from using a predetermined value of K is $0.05 \times 0.03 \times 0.02$ or 0.000 030, which is safely negligible even with the highest precision, 0.0003 as here reckoned, ordinarily sought in calorimetry. Indeed, the precision of which (14) is capable is too great to be attained without special attention to the environing temperature. There is, then, no need of using the Regnault-Pfaundler method, with its two rating periods, save in exceptional cases.

Unappreciated Advantages of the Methods of Straightforward Determination of the Temperature Loss.

The essential thing underlying formulas 7, 13, and 14 is the measuring of a temperature loss, that in the rating period, very nearly equal to that in the experimental period so that only a small difference remains subject to the uncertainties of reckoning. Formula 14 does not produce this situation, but merely takes advantage of it to avoid one rating period. The advantage in regard to precision which it confers is present, regardless of the formula that is used.

[5] White, Walter P., *J. Am. Chem. Soc.*, **48**, 1147 (1926).

[6] This may seem inconsistent with page 54 of Section 4. But there the flow of heat to the calorimeter from the hot body is the only thing considered. The resulting thermal head is affected by the thermal leakage also, and by increase in the jacket temperature, which therefore may be beneficial where the second Geophysical Laboratory method is desirable. In a considerable number of determinations with a calorimeter of $K = 0.002$, approximately, where the data for each experiment were worked up for several different couples of periods, the difference $\varphi_x - \varphi_r$, changed sign, passing thru zero, as the period length increased from 10 to 15 minutes, and was never over 0.025 for either 10 or 15.

From this it follows that the ordinary straightforward calorimetric procedure usually really constitutes a compensation method, comparable with such special methods as Person's and Richards's adiabatic, and Joule's twin calorimeters. The adiabatic calorimeter seeks to eliminate the thermal leakage by adjusting the jacket temperature. Two bodies of different character are thus kept at equality, by a manipulation calling for some quickness. The twin calorimeters eliminate the effect of the leakage by balancing it in two very similar bodies, whose slight differences can be carefully studied. The straightforward method compares the leakage with the practically equal leakage of the *same* body 5 or 10 minutes later. The difference in it is one of time, and the error due to lapse of time can be diminished almost indefinitely by either regulating the surrounding temperature or measuring it, procedures no more difficult than some which are required with the other two methods.

This view of the straightforward method seems to justify those who have claimed that with it the thermal leakage proper [7] is usually a minor source of error in calorimetry. It also accounts for the opposite claim if we suppose that those who have made that were thinking of calorimeters where the environing temperature received little or no attention, and evaporation was not controlled.

When φ_x and φ_r are not very nearly equal, the comparison with the adiabatic and twin methods is less striking, but the precision which that comparison shows to be probable is not necessarily much altered by the resulting increase in the size of the $\frac{V_r - V_a}{\theta_r - \theta_a}(\theta_x - \theta_r)$ term. The chief errors, as listed in Section 12 (page 108), are not greatly altered.

Section 3. Corollaries to the Formulas

The mere mathematical form of the temperature loss formulas just given leads directly to important conclusions regarding precision or efficiency.

Negligible Thermometric Error of the Thermal Head Measurements

The expression $\frac{\varphi_x}{\varphi_r}$ of (6) and corresponding expressions in the other formulas are multiplied by the quantity KT_x, whose value is usually not over 0.03, hence all errors in it are correspondingly reduced.

[7] *I.e.*, not including evaporation.

In ordinary short determinations, therefore, there need never be any difficulty in getting excessive thermometric precision in observations of the thermal head. In very long experiments, however, KT_x may exceed unity, and the net final precision of the thermal head measurement will then be more important than that of the temperature rise measurement. The timing of the measurements dealing with the thermal head needs to be as accurate as of those giving the temperature change. This will be discussed later, page 58.

Precision Needed in Rate Measurement

As (6) and (11) show, the temperature change $\Theta_3 - \Theta_4$, observed in the rating period, is usually multiplied by a factor nearly equal to unity when the periods are of equal length. Hence an error in this measurement has the same importance as one in the measurement of the temperature rise. The rating measurements, therefore, demand maximum precision. It also follows that the necessity of making these measurements in order to find the temperature loss usually doubles the possible accidental thermometric error, which is often the largest error connected with the calorimeter. This necessity may be said to introduce an error due to the thermal leakage. The same necessity occurs also in the adiabatic method, and becomes evident with Joule's twins when the superior procedure introduced by Richards and Gucker [8] is employed. It disappears only when the rate for zero thermal head as well as the amount of thermal leakage proportional to thermal head, that is, w and K, are known with enough precision to render unnecessary direct observation of them. Even with the ice calorimeter, as the correction for drift it forms probably the most troublesome problem affecting that instrument. The resulting error has nothing to do with the magnitude of the constant rate, or w. Even if, as in the twin method, it is only the slight residual difference between two heats of stirring or other effects which are both small and as nearly equal as possible, nevertheless, if it has to be measured at all, it causes the accidental error of the measurement to enter with undiminished magnitude.

Preferable Length of Rating Periods

The accidental thermometric error of the rating period can in effect be diminished, however, by lengthening that period, making the error less in proportion. Or we may as well say that the error is then divided by a larger factor T_r, as appears from (8). But the gain is

[8] Richards, Theodore W., and Gucker, Frank T., Jr., *J. Am. Chem. Soc.*, **47**, 1881 (1925). See pp. 127 and 128.

seldom worth the increased time it costs. On the other hand, it may often pay to gain time by shortening the rating period, in spite of the resulting increase of error. If, by also increasing 2 or 3 times the thermometric precision, the error is kept the same as before, the whole change might appear a profitable way of saving time. An incidental advantage is that with the shortening of the r-period the whole time is reduced so that errors from change in the jacket temperature or from other changes are somewhat diminished.

Effect of Change in the Environing Temperature [9]

Since constancy of the environing temperature is required whenever, as with the Regnault-Pfaundler procedure, this temperature is not observed or regulated, the error resulting from a failure of constancy needs to be known. The order of magnitude of the error is readily seen by considering the commonest case, that in which $\varphi_x = \varphi_r$, nearly. The result is little altered if the two are taken as equal. In that case the computation will give the temperature loss in the X-period as exactly equal to that observed in the rating period. But if the environment changes from one period to the other the real temperature losses will not be equal, and the difference, which is the error, will be the change multiplied by KT_x, namely,

$$K\varepsilon T_x. \qquad (15)$$

That is, it will be the temperature loss for a thermal head equal to the change ε in mean environmental temperature between X-period and r-period. Change before or after that is of secondary importance.

Constancy Needed. The constancy needed in any given case is easily calculated. If $K = 0.003$ and T, 10 minutes, neither of which is a specially small value, the error is 0.03 times the environmental change. Then for 1 per mille precision it will be negligible, i.e., 1/10 the allowable error,[10] or 0.1 per mille, if ε is $0.0001\Delta\Theta \div 0.03$ or $0.003\Delta\Theta$. This is about 0.01° if $\Delta\Theta = 3°$. A blanketed and covered water jacket should change no more than 0.025 of the jacket-room difference in 10 min. Hence the jacket in this case should not differ from the room by more than 0.4°. If it does, the resulting error is soon undesirable, and before long, serious. The difficulty is avoided by observing the jacket temperature and correcting for its change, or by using a thermostat. For precision of 0.1 per mille one of these resources is evidently necessary, and the thermostat should be good to 0.001°, unless the time or the thermal head is smaller.

[9] White, Walter P., *Phys. Rev.*, **31**, 549 (1910), *op. cit.* Jaeger, W., and v. Steinwehr, H., *Ann. Physik*, **64**, 338 (1921).

[10] Equation **4**, page 33.

It follows that in most installations to-day the change in the jacket frequently exceeds the small value here estimated to be desirable. But this will seldom come to the attention of the experimenter.

Effect of Water-Jacket Temperature Change Caused by the Calorimeter. If R is the ratio of the heat capacities of water jacket and calorimeter, the heat whose escape causes a temperature loss of $KT_x\Delta\Theta$, nearly, will cause a rise in the jacket of $KT_x\Delta\Theta\frac{1}{R}$ and the error due to this, with the jacket assumed to be constant, is, by **(15)**: $(KT_x)^2\Delta\Theta\frac{1}{R}$.

But $(KT_x)^2$ will seldom exceed 0.001, hence for 1 per mille precision, or each major error not [11] over $0.0001\Delta\Theta$, it is sufficient if the jacket holds 10 times as much water as the calorimeter. For a 5-minute period or for $K = 0.0015$ $(KT_x^2 = 0.00023)$ it might hold only 2.5 as much. For higher precision the jacket should have correspondingly greater capacity. The error, whatever it is, disappears between calibration and application if the length of period and the temperature pattern are the same, but appears in the results when either of these changes.

For a 3-liter calorimeter the value of KT_x should not exceed 0.002, so the jacket may bear a smaller ratio to the calorimeter, but such a ratio to a larger calorimeter will result in a jacket of about the same volume.

On the whole, it appears that change in water-jacket temperature resulting from calorimeter change is less serious than that due to the effect of the room, since jackets holding 20 liters are usually not at all inconvenient.

The conclusions of this section evidently apply only when the jacket temperature is not regulated or observed.

Change in jacket temperature alters some of the lag effects. (Section 10.) But the actual amount of this error is nearly always quite negligible. (See page 92.)

The Value of Partly Negative Thermal Heads (Microcephalous Method)

There is a method, considerably used and highly recommended,[12] of making the mean φ_x nearly zero by having the initial calorimeter temperature somewhat below that of the environment, passing above

[11] Equation **4**.
[12] Report of the Joint Committee on Coal Analyses, *J. Ind. Eng. Chem.*, **9**, 106 (1917).

it as the heat is added. The resulting temperature pattern is shown in Figure 4, where φ_x is the arithmetical difference of the two shaded areas. This is sometimes referred to as "Rumford's method." Rumford, however, arranged so that his room temperature was the mean of the initial and final calorimeter temperatures, in experiments with a linear rise, and paid no further attention to thermal leakage—a simple and satisfactory method for work of rather low accuracy. This other

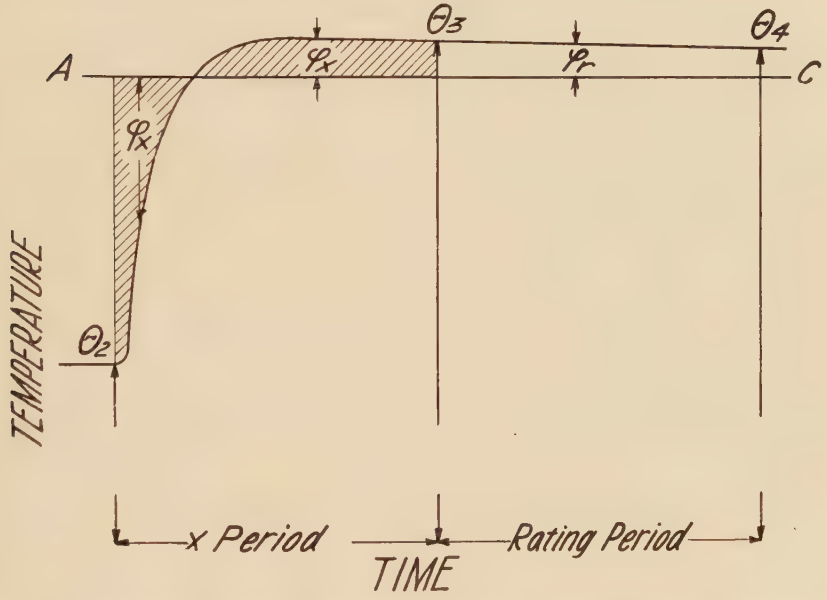

FIG. 4.—Temperature pattern of the microcephalous method, or method with small [resultant thermal] head in the experimental period (X-period).

method is recommended as an improvement where the regular 3-period Regnault-Pfaundler is used. Its special characteristic is simply the small net thermal head, whence it may perhaps be called the microcephalous method until a better name is offered.

Apparently its supposed advantage in such use rests on nothing more than the inference that if thermal leakage causes error, that error must be less if the net amount of thermal leakage is made less.[13] At any rate, examination readily shows that the advantages of the method, when applied to the Regnault-Pfaundler procedure, are slight, and far less than the drawbacks.

[13] It is said (report just cited) that the method is superior because the total thermal leakage and the total evaporation are less. In this claim the probable size of the *errors* is not considered.

It has been pointed out that in applying (13) the temperature loss is ordinarily the single observed difference $\Theta_3 - \Theta_4$, modified by another small calculated term whose final error is very small. The method with small φ_x, as a rule, deliberately destroys this advantageous condition, getting its small resultant temperature loss as the difference between $\Theta_3 - \Theta_4$ and a compound term nearly as large as $\Theta_3 - \Theta_4$. Thus it is incompatible with the second Geophysical Laboratory method, and so, in spite of its approximate elimination of K as a factor, is one of the longest methods in use. This disadvantage, however, has only appeared since the value of the Geophysical Laboratory method has been pointed out.

How far the microcephalous method diminishes the error in finding the temperature loss can be seen by rearranging the temperature loss formula so that it reads:

$$\frac{V_r(\theta_x - \theta_a) + V_a(\theta_r - \theta_x)}{\theta_r - \theta_a} \qquad (16)$$

Error in the thermal head readings is practically confined to error in θ_x coming from difficulty in following the temperature rise. It is easy to show that the effect of an error, ε, in θ_x is nearly $KT\varepsilon$, about the same for both methods, as common sense would lead us to expect. Errors in the rates, V_a and V_r, are the errors of thermometric observations, are accidental, and are likely to be as large in V_r as in V_a. Ordinarily, the final error from them is very nearly the error in V_r alone. With φ_x nearly zero the error in V_a has a multiplier of appreciable value; but the multiplier of V_r, namely $\frac{\theta_x - \theta_a}{\theta_r - \theta_a}$, will usually be from 0.7 to 0.9 or more, hence the error in V_r will still preponderate. About half the time the two errors will have opposite signs, hence the probable error will be a little smaller than if φ_x nearly equals φ_r. Not the probable error, however, but the largest error that is at all probable, has been said (pages 30, 31) to be important in practical calorimetry. This error may be taken as occurring when large errors occur in V_r, since coincidences in large errors in both V_r and V_a will be rare, and not specially influential when they occur.

The effect of the thermometric rating-period error, then, is reduced by this method, but usually not below 0.8, or no more than it could be by lengthening the rating period a minute or two.

A gain arises in certain cases because the instantaneous value of φ_x is never so far from zero, hence there will be less variation in the

value of K, the thermal leakage modulus. This slight advantage will be appraised in the section on that modulus.

These advantages, such as they are, are greater when the temperature rise is gradual, so that $\theta_x - \theta_a$ is nearly equal to $\theta_r - \theta_x$ (a condition approached in electric calibration) because then the multiplier, $\frac{\theta_x - \theta_a}{\theta_r - \theta_a}$ of the error in V_r is nearer one-half. But at most the gain is only the elimination of half the rating period error, or one-fourth of the total thermometric error.

Against these minor advantages is to be put, besides the exclusion of the valuable second Geophysical Laboratory method, a second very serious disadvantage,[14] that evaporation makes the effective leakage modulus different when the calorimeter temperature goes below that of the jacket. This makes real precision hopeless without a correction for the change in an uncovered calorimeter, and uncertain when the correction is attempted; while the greater precision proper to a well-covered calorimeter can be jeopardized by a slight condensation on the surface while the calorimeter is colder.

A third disadvantage of the microcephalous method, less serious, but outweighing the advantages, occurs when objects are dropped into the calorimeter at the beginning of the X-period. This changes the value of the modulus, K. If fK is the amount of change, it is easy to show that the error is:

$$\frac{fV_a}{\theta_r - \theta_a}(\theta_x - \theta_r)T_x \qquad (17)$$

This is small ordinarily, since both V_a and $\theta_x - \theta_r$ are ordinarily small. The method with φ_x near zero makes V_a very large and $\theta_x - \theta_r$ rather large.

Unless some error in the foregoing reasoning can be pointed out, therefore, it would seem that the sooner the microcephalous method is forgotten, the better.

Section 4. The Thermal Head

The *Thermal Head,* as already stated, is that difference of temperature between calorimeter and environment which causes the thermal leakage. With a completely inclosed calorimeter it can be directly measured; otherwise its value must be inferred from the heat flow it causes; but its determination or use thru calculations demands that the environment be constant.

[14] Richards, T. W., and Burgess, L. L., *J. Am. Chem. Soc.,* **32**, 449 (1910).

The thermal head is proportional to the main temperature loss, and successive improvements in controlling it have formed one line of development in modern calorimetry. These improvements have mainly consisted in making the thermal head more definite.

Thermometric errors, as has been shown (p. 43), are far from dangerous as far as thermal head is concerned.

Zero Thermal Head Methods

Of secondary importance, also, is the smallness of the thermal head. One method, the microcephalous, for making the thermal head small, is positively detrimental (*see* Section 3 § 5); the chief one, the adiabatic, obtains its advantages in indirect ways. The notion that diminishing the thermal head necessarily diminishes thermal head error, in view of its incorrectness and its prevalence, perhaps deserves to be called "The Calorimetric Fallacy." [15]

The reason why this notion is false has already been indicated in part. The thermal leakage follows a definite law, and generally shows no irregularity within the time of an ordinary experiment. The temperature loss determination is a comparison with the temperature loss in the last rating period; the difference between the two losses, the only thing involving calculation or assumption, is small. Such errors as there may be, therefore, come from irregularities, which are elsewhere than in the law of the thermal leakage. Moreover, these irregularities are apt to be increased by the measures taken to bring the thermal head to zero.

Definiteness of Thermal Head

The importance of definiteness in the thermal head has been appreciated more or less completely for a long time. The simplest rule for attaining it was stated some time ago,[16] namely, that the thermal leakage should take place between two bodies only, each of which is entirely at a uniform temperature. These bodies are, of course, the calorimeter and a completely inclosing jacket.

Definiteness in the Jacket. On the part of the jacket completeness is ordinarily the only thing demanding much care or contrivance, and

[15] To guard against possible, if improbable, misunderstanding, it may be well to say that this does not apply to those writers, such as Theodore W. Richards, who, recognizing that a continuously small thermal head lessens convection and evaporation errors, have expressed this briefly by saying that it lessens thermal leakage errors. The fallacy is in saying that *the* thermal leakage error, that is, all the errors, are lessened. The majority are not, and are often allowed to be needlessly large while the thermal head is made small. Typical instances of the calorimetric fallacy are advocacy of the inferior microcephalous method, and the remark, not so very rare, that a very small air gap does no harm in the adiabatic method, because the adiabaticity cuts out all leakage error, anyway. Most of those making this remark would doubtless shy at its logical conclusion, which is that the calorimeter might as well be in direct contact with the jacket. *See also* page 111.

[16] White, Walter P., *Phys. Rev.*, **31**, 550 (1910).

this has but one feature of difficulty—the jacket cover. Water jackets protecting the calorimeter fully at sides and bottom are the rule at present. Entirely satisfactory covers involving comparatively little difficulty have been provided by the invention of the "submarine" and the "water cap" (Section 21), while the double copper cover recently proposed (Section 21) is almost as satisfactory thermally, and yet is about as inexpensive and as convenient to manipulate as any cover could possibly be. Covers of uncertain and lagging temperature, such as those of wood or hard rubber, seem now to have no justification save that of being sometimes good enough, and already in use.

Uniformity of jacket temperature is, outside of adiabatic work, easy to secure in abundance. This is shown, for ordinary calorimetry, by the success of adiabatic methods, where the rate of jacket temperature change, and therefore the difficulty of securing uniformity, is usually over 100 times as great as usual. The experimenter thus should have no need to give special attention to jacket temperature equalization and is pretty sure not to do so. For that very reason, however, its adequacy should be beyond question. A certain bomb calorimeter jacket, consisting, at the side, of an annular trough 4 cm. wide, stirred by a propeller making 600 revolutions per minute in a tube of 2.5 cm. diameter, showed between top and bottom a difference about 1.2 per mille of the jacket-to-room difference. After the upper part of the water had been heated, about 3 minutes were required for the stirring to reduce the temperature difference to 1 per mille of its original value.

Assuming that the stirring just described was sufficient, stirring about 4 times as efficient seems desirable in order to insure having enough under all conditions, since the fourfold stirring is quite easy to get. A propeller tube of twice the diameter is all that is needed to get it. Room for that may be obtained by doubling the thickness of the annular trough, which also makes the jacket temperature more constant. The calorimeter chamber can also be set eccentrically according to the method described (p. 71) under Calorimeter Stirring. The same principles apply with all jackets. Stirrers of greater diameter than are ordinarily used cost practically nothing extra, in cash or convenience, and increase very rapidly in efficiency as their size becomes larger. From 8 to 14 cm. seem desirable diameters in most cases.

The irregularities which stirring corrects are greatly diminished if the jacket is blanketed and if evaporation is largely prevented. Since these two things are very easily done, it is nearly always a mistake not to attend to them.

Apparently a still stronger reason for restricting evaporation lies in the desirability of insuring that the wall of the calorimeter chamber, when it is supposed to be dry, should not have adsorbed any vapor coming from the jacket water. (See Section 11, on evaporation.)

Stirring in Adiabatic Calorimetry. Within tanks not over 30 cm. in diameter with short and wide paths for the water, lags of from 4 to 14 seconds are likely to exist, even with decidedly vigorous stirring; that is, stirring which is on the point of splashing the water about from an 8 cm. stirrer tube. Hence studies of the jacket temperature distribution have been made by some workers,[17] and would seem to be worth while in all attempts at very precise adiabatic calorimetry. They are far more readily made with electric thermometers; and differential measurements between different parts of the bath during heating are decidedly preferable.

Distribution of the heat sources through the bath, as practised by several experimenters, is evidently advantageous, and a distribution of the thermometers over the surface of the calorimeter chamber seems desirable also, and is not difficult with electric thermometers. Even with a single thermometer and heater, however, the resulting tempertaure lags, positive or negative, will be largely eliminated between calibration and application. Hence it is sufficient if the lag effect is not more than a few times the tolerable single error, and particularly if the speed of stirring and other arrangements are not allowed to be changed, so that the lags may be constant. The loosening of a belt, for instance, by changing the speed of jacket stirring, and hence some lags, may cause an error with the adiabatic method.

Definite Calorimeter Temperature. On the part of the calorimeter, definiteness of thermal head calls, as with the jacket, for stirring adequate in amount and properly designed. In earlier articles of Dickinson's and mine, the maximum absence of lagging parts was also emphasized. A more thorough study of lags has since indicated that small lags may do no harm in calorimeters experimentally calibrated. Greater freedom may thus be obtained in using covers to prevent evaporation. Such covers will be discussed in detail.

Thermal Head Measurement

With Thermostats. A thermostat may be used in the jacket to avoid the necessity of watching the temperature. Even if the thermostat is constant only to 0.01° for 20 minutes, a leakage modulus, K,

[17] *E.g.* Richards, T. W., and Jesse, R. H., Jr., *J. Am. Chem. Soc.*, **32**, 274 (1910).

of 0.002 would give a maximum error from uncertainty of thermostat temperature of $0.002 \times 0.01° \times 10$, or 0.0002°, which is quite good enough for precision a little better than 1 per mille.

On the other hand, in work to 0.1 per mille, while a thermostat may often be very convenient,[18] direct measurement of jacket temperature is likely still to be necessary. But the slight fluctuation of temperature, as the heat goes off and on, makes any single observation of thermostat temperature likely to be misleading. To avoid this trouble by multiplying observations is a bother, and may be inadmissible. The oscillations may be made quick and small by modifying the regulator, or lag may be added to the thermometer[19] by surrounding it with a rubber tube or a test tube full of water. Such a source of lag is easily made removable to facilitate quick adjustment of temperature, as in the adiabatic X-period. The lag should not be too large, but a relatively large one may do no harm in a thermostat.

Calorimeter Temperature and the Length of the X-Period. Four processes are distinguishable in the temperature pattern of the X-period: (1) The introduction or production of the heat; instantaneous, where a hot body is dropped into the calorimeter; nearly instantaneous with some chemical reactions, protracted, and tending to die away gradually, with others; uniform, with abrupt beginning and end, in electric calibration. (2) The communication of the heat to the water; very brief where a reaction takes place in the water; an exponential curve, and the chief feature of the temperature pattern, if hot bodies are dropped in, and in combustion calorimetry, where the massive bomb gives out heat. (3) The giving of heat to outlying parts of the calorimeter; very small, and often imperceptible; exponential, but of opposite sign to (2). (4) The cooling of the calorimeter as a whole by thermal leakage. This is exponential, but so slow that it is commonly treated as linear over periods of 10 minutes.

If exception is made of electric calibration, which is in a class by itself, it thus appears that the temperature rise, when not very brief, is usually almost truly exponential. The equation of a simple exponential rise is: $\Theta = A\ (1 - e^{-\frac{t}{\tau}})$, represented by Figure 5, where A is the final value and τ a time indicating the rate at which this final value is reached, more definitely the time at which the exponential term equals $\frac{A}{e}$. The integral to infinity of this term (shaded area in the

[18] White, Walter P., *J. Am. Chem. Soc.*, **36**, 2320 (1914).
[19] *Ibid.* p. 2321.

figure) is $A\tau$, hence the integral under the curve for an indefinitely long time, T, is

$$A(T-\tau). \qquad (18)$$

For temperature rise curves that are approximately exponential, the necessary length of the X-period can be determined by assuming that they are exactly so. The X-period should end when practically all the heat has been communicated to the calorimeter; that is, when the difference between the curve and its asymptote is $0.0001A$ or

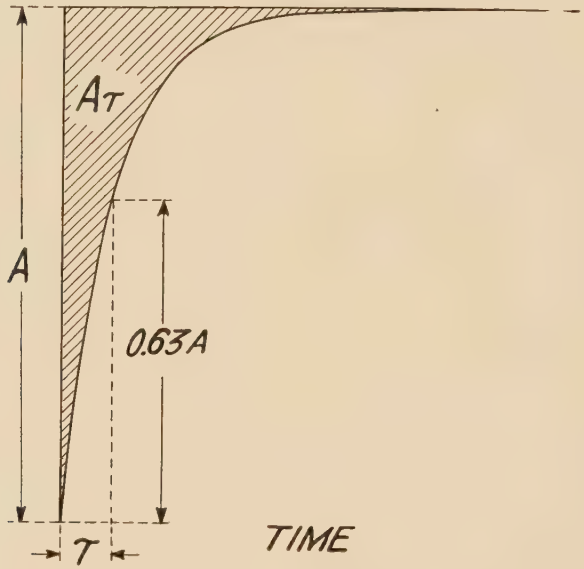

FIG. 5.—Diagram illustrating some properties of an exponential curve.

$0.00001A$ for precisions of 1 and 0.1 per mille, according to equation 4. This will occur when the time is, approximately, 9τ or 11τ. And τ is the time when the temperature rise is 0.63 times the final. The rise is 0.8 times the final when $t = 1.6\tau$ or $\frac{8}{5}\tau$, hence for 1 per mille precision the time should be 6 times that needed for 0.8 rise, or, it may be as short as 5 minutes only if 0.8 rise is completed in about 54 seconds. But in such calculations the time should be reckoned from the zero of the exponential curve, which may be a little later than the starting of the reaction.

It is easy to see that the X-period should not be considered at an end when the temperature ceases to rise. For heat is then being com-

municated to the calorimeter water at a rate equal to the cooling rate, and considerable heat, therefore, still remains to be transferred.

A smaller error may result if the period is treated as ended when the cooling rate first appears to be constant. For the determination of this instant may involve an error of the order of twice the accidental error of an observation. And since the rate on an exponential curve equals the ordinate divided by τ, the deficiency of calorimeter temperature may be τ times the error made in estimating the slope of the curve, and this deficiency enters twice, in X-period and rating period. It is therefore well to end the X-period 2τ (usually not over 2 minutes) after the apparent linear rate seems to be attained, when any error there may have been will be diminished to 1/10.

It is also possible to observe the asymptotic approach of the initial rate to the final cooling rate where the initial rate is larger, a few minutes before it becomes doubtfully negligible, and then extrapolate to the negligible point. The effect of the observational error is thus greatly reduced, while the chance of introducing any other error is exceedingly remote.

The proper length of period can also be determined,[20] without any hypothesis as to the type of temperature rise, by taking enough observations so that several sets of periods, of different lengths, can be calculated for the same experiment, and periods thus found such that further length does not increase the total temperature rise as determined.

Measuring the Calorimeter Temperatures During the Temperature Rise. In most presentations of the Regnault-Pfaundler formula the directions for obtaining the $\int\theta_x$, or temperature for the X-period (experimental period, or period of temperature rise), are as follows. A series of observations, $a, b \ldots . z$ is taken. The first part of the period, from a to b, has a mean temperature of $\frac{a+b}{2}$, the next, of $\frac{b+c}{2}$, etc. Adding all these, we get: $a+b+c\ldots .+z-\frac{a+z}{2}$ which is the period temperature required. This procedure gives the area of a polygon, $abc\ldots .z$, Figure 6, which is less than the true area by the sum of the segments ab, bc, etc. This is where readings are made at the beginning and end of the X-period. If the period is divided into parts with an observation taken at the mid point of each, the resulting sum is a little greater than the true value represented by the area under the curve. It is quite legitimate to measure one part of the X-period in one of these ways, the other part in the other. I

[20] Bohn, C., *Pogg. Ann.*, 122, 296 (1864); White, W. P., *Am. J. Sci.* 47, 54 (1919).

have usually found it convenient to do that. Labor is saved also by observing [21] the latter part of the X-period temperature curve less often than is necessary in the earlier, more sharply curved part.

Simpson's Rule and the X-Period Temperatures. It is necessary to measure often enough in the X-period so that the segments *ab, bc,* etc., of Figure 6 do not constitute an appreciable error. For those who prefer to substitute a very little more of calculation for some of the observing it is possible to integrate the curve very closely

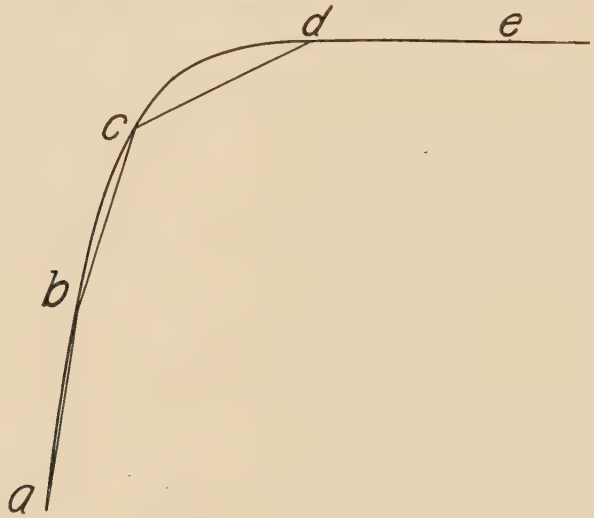

FIG. 6.—Diagram accompanying the discussion of measurement of the temperature rise curve.

by applying smaller curves to it instead of straight lines, yet using fewer points. Simpson's Rule [22] is admirable for this purpose. Since the formulas it gives are rigorous for binomials, they apply very well to the usual temperature rise curve,[23] which, as has been shown, is approximately exponential. If 3 observations *a, b, c,* define 2 intervals on the curve, Simpson's formula

$$(a + 4b + c) \div 6 \qquad \textbf{(19a)}$$

gives the average ordinate of the area; for points at the middle of each of 3 intervals

$$(3a + 2b + 3c) \div 8 \qquad \textbf{(19b)}$$

gives the same. Two applications of the first formula, involving 5 points, to 2 pairs of intervals, will very often be sufficient. The

[21] White, Walter P., *Phys. Rev.,* **31**, 552 (1910).
[22] Ency. Brit. 11th Ed., Vol. **18**, p. 143.
[23] White, Walter P., *J. Am. Chem. Soc.,* **48**, 1148 (1926).

method, however, usually will not allow the experimenter to escape from the necessity of taking 2 points on the steep part of the curve, since a displacement of any considerable part of that curve by 1 second is equivalent to an uncompensated lag of corresponding amount.

The reasoning of the preceding two paragraphs evidently does not apply well to a linear rise, such as is given by electric heating. Such rises, however, are easier to follow than those approximately exponential. See Section 20.

Dickinson's X-period Method. Dickinson[24] has described a method based on equation (18). The time when 63 per cent of the rise is reached is the only observation needed during the X-period. This time, τ, gives at once the desired area, $A(T - \tau)$. The method assumes an exponential curve; it can be used by making an empirical correction for slight variations from the exponential, most successfully in series of observations on similar material; it is particularly well adapted to the resistance thermometer,[25] as now ordinarily employed.

If there is doubt as to the adequacy of the method, which, of course, means doubt as to the similarity of the temperature patterns in different experiments, a comparison with results from fuller data in special runs will show how great precision is being attained. This check, however, is evidently useless whenever the experimenter's reason for desiring Dickinson's Method is because he is not in a position to make complete observations.

New Combination Method, Based on Dickinson's. In such cases, and as a regular procedure where Dickinson's Method proves to be inadequate and complete observations are difficult, there seems to be no doubt that a combination method would be valuable; reading the rapid rise by Dickinson's method, and then, at the end of one, two, or more minutes, beginning regular observations at minute- or half-minute intervals. The uncertainty from assuming a uniform departure from an exponential curve is thus confined to an arc which is both much smaller and nearer to the observation. It might also be useful to use the later observations to give a correction of the area as found from the single time observation in the rapid rise. This could perhaps best be done by comparing one or more of the later observations with the exponential curve extrapolated from the single one. This procedure, tho it might require reference to a table of exponentials, is,

[24] Dickinson, H. C., U. S. Bur. Standards Bull. 11, 230 (1914).

[25] I have shown, however [*J. Am. Chem. Soc.*, 48, 1148 (1926)], that there are several reasons why the resistance thermometer should be used in a way that makes it less dependent upon this method.

after all, not very laborious, and would unquestionably be justified if nothing else would give the required precision.

This method is in one respect the exact opposite of Dickinson's. That is a labor-saving method, with possible sacrifice of precision; this will seldom save any labor, but may give a precision not otherwise attainable under some conditions.

I believe this method is here presented for the first time.

Section 5. Timing

Precision Needed

Except in adiabatic work all temperature observations are made at definite instants of time, and are therefore combined time-and-temperature measurements. A corollary to Lag Equation (L2) (page 87) is that the same time precision is needed in the X-period, where the thermal head is determined, as in the readings of temperature rise and rate. If V is rate, and $\Delta\Theta$ temperature rise, the final effect of a time error, ε, is rate times that error, or

$$V_r\varepsilon = K\Delta\Theta\varepsilon, \tag{20a}$$

approximately, in the terminal temperatures, and leakage modulus times time and temperature error, or modulus times time, rate, and timing error, or

$$K(\Sigma V_x T)\varepsilon = K\Delta\Theta\varepsilon, \tag{20b}$$

again, in the X-period. The more rapid rate makes equal time precision correspond to a much less temperature precision in the X-period, as has already been shown (p. 43) in a different way. But this inferior temperature precision, being multiplied by the small quantity, K, gives an equal final precision. The apparent temperature irregularities in reading a rapid rate are not only usually negligible in themselves, they are not really temperature errors at all, but disguised time errors.

But the timing precision must be adequate. If K is 0.003 then the error will be 1 per mille if ε is 1/3, that is, 20 seconds. Hence timing error, to be safely negligible, must be as small as 2 seconds for 1 per mille precision.

For high precision K should be, and usually can be, made at least as small as 0.0015. Then, even for 0.1 per mille precision, the timing need not be to less than 0.4 second, while for 0.3 mille precision, probably the best yet reported, timing to 1 second suffices. For these degrees of precision a time signal to the ear is very desirable, tho hardly essential for 0.3 per mille.

In some experiments where a wide range of calorimeter rates was timed, both by ear signals, involving estimation of tenths on a galvanometer scale, and by recording on a chronograph the time when even divisions of the scale were passed, it appeared that errors of 0.1 second were somewhat more frequent than errors of 0.1 scale division. A fair approximation for the probable errors in these experiments is 0.05 second, and 0.03 scale division.

Timing of the Terminal Temperatures

Of the temperature readings demanding maximum precision, namely, those at the ends of the periods, which give the temperature rise and the rate, two will normally be made when the rate is about $K\Delta\Theta$, where $\Delta\Theta$ is the temperature rise. The timing error in these, on the basis of 0.05 second and $K = 0.003$ per minute, will therefore be $0.000\,002\,5\Delta\Theta$, or for a rise, $\Delta\Theta$, of 4°, 0.000 01°. This is 1/3 the probable error in reading the most sensitive electric thermometers ordinarily used. For a rise of 12°, or for threefold relative thermometric precision obtained in any other way, the timing error would equal the other.[26] But a diminution of K, desirable on other grounds with so very high precision, would reduce the timing error.

Timing in the Temperature Rise

Experimenter's Lag. The timing errors known as lags, which come from the temperature distributing mechanism, are usually constant. A true lag will affect all readings by the same number of seconds, and can be treated as a single quantity. But timing errors in reading are accidental; that is, continually variable. They also depend on the care and attention exercised by the observer. It is therefore of some importance to know when the observations need special attention. This is only during the more rapid parts of the rise. So much, indeed, is likely to strike anyone who actually reads the thermal heads. When the temperature is nearly stationary, its reading is not much affected by slight changes in the instant of observation. What may not be so obvious, however, is that the cruder timing is permissible only where the rate is slower than elsewhere. The timing error is $\varepsilon K\Delta\Theta$, and ε may be large only when it does not multiply a large part of the rise, $\Delta\Theta$. A uniform rise, no matter how slow, must, on the whole, be timed as accurately as a rapid one. The smaller temperature error of each observation is fully compensated by the greater number

[26] The extraordinary precision obtainable with twin calorimeters, however, not only does not demand especially accurate timing, but is consistent with very crude timing, since the differential temperatures measured are varying very slowly.

of observations in the protracted curve which results from the slower rate. A small part of a long, slow rise may have crude timing, but most of it must be timed carefully. When one part of the rise is much more rapid than the rest, as is nearly always the case, the rest is usually a small part of the total, and if so, may be timed less strenuously. This possibility relieves labor in adiabatic calorimetry.

Variable Stirring During the Temperature Rise. More important is a corollary to the preceding. Since the distribution of temperature in the calorimeter by stirring possesses a true lag, and the effect of lag is $LK\Delta\Theta$, corresponding to $\varepsilon K\Delta\Theta$ (Equations **L2** (page 87), and **20**), the lag may be increased, that is, the stirring may be slowed down, as soon as a rapid and major portion of the rise is ended.[27] The heat of the slow stirring is negligible, absolutely or relatively, and the possible error from the heat of the more rapid stirring is correspondingly diminished. Such a reduction of stirring speed in the adiabatic rating period also is advantageous and may be easier in manipulation; its extension into the X-period makes the heat production a third to an eighth of what it would otherwise be.

This change to a low speed seems admissible only when all rates are very near zero. The opportunity of resorting to it may thus be regarded as an advantage of the adiabatic method. In ordinary working the lags of the terminal temperature and rate determination would be most undesirably increased, the thermometer lag compensation jeopardized, and the compensation of the L_2K effect destroyed. (Equation **L3b,** page 89.)

Instead of slowing down the stirring, Barry [28] stopped it altogether, starting it again before each reading. This method goes with simpler apparatus, and is not excessively laborious. It is unimpeachable if, like Barry, the experimenter takes pains to determine the slight error involved. The test is not hard to make.

Barry and I have found that tho a very slow propeller stirrer often seems to produce no result, it does move the water at a rate proportional to its own speed.

A two-speed governed geared stirring arrangement now in use in the Geophysical Laboratory, tho effective, cost more to make than had been anticipated. Hence the best way to get a lower speed is probably to make it so low that no great constancy in it is needed, and then run it either by changing to a simple pulley-and-string drive, or by putting resistance in the circuit of a governed motor so that the

[27] White, Walter P., *J. Am. Chem. Soc.,* **40**, 1893 (1918). Barry, F., *ibid.,* **42**, 1934 (1920).

[28] *J. Am. Chem. Soc.,* **44**, 911 (1922).

speed drops well below that at which the governor is operative. This paragraph is not intended to imply that a pulley drive may not be adequate for a constant higher speed.

Retarded Reactions. The same principles apply to the question of increasing the time of thermochemical reactions, in order to avoid a very rapid temperature rise. This rapid rise, as such, does not cause any greater error from either the experimenter's possible slowness or the lag of the stirring. The rule that the error equals $\varepsilon K \Delta\Theta$ or $LK\Delta\Theta$ (Equations **20** and **L2**, page 87) applies to both.

There are reasons, tho, why a protraction of the reaction may sometimes be advantageous. (*a*) If, in adiabatic working, the rate of jacket heating is limited, it may be well to hold back the calorimeter temperature so that that of the jacket can rise with it. (*b*) A very sudden rise may be hard to measure in non-adiabatic work. Previous demonstrations regarding lag effects have almost universally involved the assumption that the temperature pattern is completely described by the observations. In general, more than one observation during the rapid rise is necessary for this. A very sudden rise, coming in the interval between two observations, may have its time uncertain by the interval between the two. This may correspond to an error of 0.7 per mille. The difficulty may be avoidable by knowing the form of the rise, and then either watching for it or knowing its time from the manipulation. (*c*) In adiabatic work a slower rise may be more accurately duplicated in the jacket. The experimenter, to be sure, will watch for the rapid rise, and can follow it with no more than the normal heater lag. But in a slower rise the first reading gives warning for the other adjustments, enabling them to anticipate the heater lag, and even to compensate for the delay of the first adjustment.

Section 6. The Cooling Rate, and the Accurate Temperatures

The magnitude of the cooling rate, V, of the calorimeter affects the temperature loss and the lag errors, but these are most simply and effectively discussed in connection with the things, such as the thermal leakage modulus, K, which determine the rate.

There remains only the measurement of the rate. This depends simply on the time-and-temperature measurements at the ends of the rating periods. These, it has been shown (page 44) require the same precision as the measurements of the temperature rise. One measurement, or with two rating periods, two, is common to both rate and rise. Affecting both, it counts twice, and so, in its contribution to the probable error, is equivalent to four, since each single error is squared in finding

the probable error of the whole experiment, and the square of a double error is four times the square of a single one. Hence there is the equivalent of 6 accurate temperature-time measurements, each of whose errors is nearly unchanged in the final result. Much the same is true also for 2 rating periods, as (16) shows.

Size of the Temperature Error

From this, taking the estimate, given in the preceding section, of 0.03 scale division as the probable error of a single temperature observation, it follows that the probable error of an experiment, as far as this is due to temperature measurement, is $0.03 \times \sqrt{6}$, or 0.074, scale division. Since it is desirable (*see* page 32, above) to have the probable error one-third of the allowable, the allowable error cannot be less than 0.22 scale division, or the scale division not more than 4.5 times the allowable error. Hence, to be fairly sure of 1 per mille precision with a mercury thermometer graduated to 0.01°, or of 0.1 per mille with an electric thermometer with the scale division corresponding to 0.001°, the temperature rise must be $0.01° \div (0.001 \times 4.5) = 2.2°$. On account of the factor of safety already shown to be desirable in this particular reckoning (*see* page 32, above), it would be safer to say 4°. This result assumes the averaging of 2 parallel experiments, where an error of $3R$ is theoretically exceeded only a few times in 1000; for single experiments, where it is an error a little over $4R$ which should be exceeded as often, the safe temperature rise would be some 40 per cent greater.

The Chief Error Usually in Temperature Measurement. It may now begin to be clear why it is the temperature measurement that usually sets the limit of precision in properly planned calorimetry. For it is more of an undertaking, in cruder work, to substitute electric for mercury thermometers, than to deal adequately with the other sources of error, as has already been seen in the sections on thermal head and timing, and will be in other sections. And in the most refined work a similar situation prevails, altho the other sources of error now need far more attention.

A possible exception to this last statement is the case of a very sensitive differentially-used thermel [29] with twin calorimeters. This certainly can give nearly or quite tenfold thermometric precision with comparative ease, but the arrangement diminishes some of the other errors also.

[29] "Thermel" = "thermoelectric thermometer." *See* White, Walter P., *Science*, 55, 617-618 (1922).

Effect of Other Errors. Since the probable error of the sum of a number of equal errors is proportional to the square root of the number, a few other errors, added to the six due to temperature reading, will not affect the final error very much, unless they are larger than those. And since any errors that are smaller will be decidedly smaller when all are squared to find the resultant probable error, most of the errors aside from the thermometric will have very little weight, even if they cannot readily be brought down to the value, one-thirtieth of the allowable error, which has been shown above (page 32) to be negligible. Error here means the error of each and every observation, multiplied by the factor by which that observation is multiplied in computing the temperature loss.

Averaging Individual Observations

The accidental error of the accurate temperatures Θ_2, Θ_3, Θ_4, which give the temperature rise and the cooling rate, can be diminished by averaging the individual readings, and this seems advisable where the greatest precision is desired, since it protracts the experiment very little, and also helps to avoid errors which are really mistakes, such as wrong recording. Separate readings 15 seconds apart are easily made, and 5 such occupy a minute. I have elsewhere [30] given a quick and easy method of averaging. As the separate observations are recorded, each is subtracted from the preceding. The time required for this is almost inappreciable, since the differences are nearly constant for one set of readings. Five readings yield four differences. If these differences, in order, are called a, b, c, d, it is easy to show that the arithmetical mean of the 5 readings differs from the middle one by

$$\frac{[a - d + 2\,(b - c)]}{5} \qquad (21)$$

a value which is almost never more than one unit of the last place, and can be obtained at a glance. Table I gives an example.

The italicized portion is inserted here as explanation, and is mental in the actual work. The third reading usually remains unchanged. In the majority of cases all the differences are the same. For three readings the average is $(b - c)/3$. The probable error is diminished, theoretically, to less than half by taking the average of five numbers, but such a gain seems practically improbable here if the average is expressed in tenths of scale divisions, since the probable error of any number so recorded, due to the recording alone, is evidently one-fourth

[30] *Phys. Rev.*, **31**, 680 (1910).

TABLE I.—Rapid Method of Averaging.

Readings	Differences	
1789.9		*Computation:* $1.2 - 1.0 = 0.2$. $1.0 - 1.1 = -0.1$
	1.0	
88.9		$2 \times 0.2 - 1 \times 0.1 = 0.3$
	1.2	
87.7	1787.8	$\frac{0.3}{5} = 0.1$
	1.0	
86.7		
	1.1	*Corrected reading* $= 1787.7 + 0.1 = 1787.8$
85.6		

scale division. The chances are better if the quotient is carried to another decimal place, and so used in further calculations. In one case where this was tried for several sets of parallel results the agreement between the experiments was improved.

The average thus obtained applies to a time later than the first reading and earlier than the last. Time is saved by correcting the first reading for Θ_3, the last for Θ_2 and Θ_4. A simple way to do this is to average the five readings as before, and then add the most probable difference between the mean and the first or last. The formula, for five readings, is, if F is either first or final:

$$F - \frac{3(a - d) + b - c}{10} \tag{22}$$

SECTION 7. THE CONSTANT RATE AND THE HEAT OF STIRRING.

The discovery that the total spontaneous change in calorimeter temperature could be expressed in the simple form $w + K\varphi$ was in its day an important advance, greatly simplifying the calculation of the temperature loss. If the expression is taken as an approximation for a complicated set of quantities, then $K\varphi$, as has been said, is a somewhat imperfect expression for the thermal leakage, plus a probably sufficient value for the combined temperature coefficient of several small effects. The rate w is the sum of all the rates in action when φ equals zero, which sum, with constant environment, is fortunately usually constant for the time of the experiment.

COMPONENTS OF THE CONSTANT RATE, w

The constant rate, w, may include, besides evaporation, some effects not ordinarily thought of at all in connection with it, such as condensations, and even oxidations. It also covers changes in thermometers, which simulate temperature rates, particularly changes (*if steady*) in the temperature of auxiliary coils of electric thermometers. But its

preponderating components are, above all, the heat produced by stirring, and secondly, the flow of heat between outer air and calorimeter which the interposed jacket does not prevent. This last has a section to itself.

The Heat of Stirring

Importance of Design. The stirring diminishes errors from uneven temperature distribution; it causes errors by irregular heat production. The sum of these errors is to be made small. It can be said, well enough for the present purpose, that the useful effect is proportional to speed, the heat, and therefore its error, to the cube of the speed.[31] It follows that the effectiveness of the stirring, the equalization for a given speed of the water, as determined by the design of the calorimeter, is much more important than the efficiency of the stirrer in the technical sense; that is, the speed developed for a given heat production. For a doubling of efficiency will, for the same equalization (or non-equalization) error, make it possible to have the heat and heat error half as great; while if the equalization is made twice as effective, so that the amount of stirring required, and therefore the speed, can be reduced to one-half, the heat and heat error will be reduced to one-eighth.

Constancy the Most Important Property of Stirring Lag. The imperfectness of temperature equalization is usually most advantageously considered as a lag. It has all the characters of a lag, namely: it is a temperature difference (of thermometer and calorimeter wall) which is proportional to the temperature rate; it can be expressed as the same number of seconds tho the rates differ; its effect is $LK\Delta\Theta$ (by (**L2**), page 87), like that of any other lag; it depends on heat flow; the only peculiarity is that the heat flow is due to forced convection. instead of to conduction, as with most other lags. Since it is a lag, its effect is eliminated when the calorimeter is experimentally calibrated, except so far as it fails to be constant.

Constancy, then, is its chief virtue; keeping it small is useful only as a means of lessening the absolute value of its variations; things, such as variation in the viscosity of the calorimetric fluid, which cause it to vary, may be more important than its magnitude.

Advantages of Small Thermal Leakage. One way to make equalization more effective is to diminish the need for it. Since the faulty-equalization error is really an error in the thermal head measurement,

[31] Richards, T. W., and Burgess, L. L., *J. Am. Chem. Soc.*, **32**, 448 (1910), *op. cit.*; White, Walter P., *Phys. Rev.*, **31**, 575 (1910) and *J. Am. Chem. Soc.*, **40**, 1880 (1918). *But see* Barry, F., *ibid.* **44**, 911 (1922).

and the thermal head φ is multiplied by the leakage modulus K, a diminution of K makes stirring less necessary. Thus a diminution of only 21 per cent in K permits the heat of stirring to be made half as great, with equalization as adequate as before. The installation of a convection shield will usually, by reducing K to about four-sevenths of the value without it, allow the heat to be made less than one-fifth. A vacuum-walled calorimeter may sometimes reduce K to one-third, or the heat to one-twenty-seventh. The same results are of course obtained by treating the error from inadequate stirring as a lag, since the lag error, by (L2), page 87, is $LK\Delta\Theta$.

These statements are not intended to imply that the experimenter will know or always need to know at all accurately how good his equalization is. But the gain from improved arrangements will be there, whether it is identified or not. And one result of a known diminution in K would be that the stirring speed could safely be reduced in proportion. The new speed would probably not be ideal, but it would be certain to be as nearly adequate as the old one was with the former value of K. In general, the advantage gained by diminishing K should be used to diminish both errors. It is readily shown that if speed is the only variable, the ideal value of it is that which makes the error from imperfect equalization 3 times that from the heat of stirring. A practical rule in sufficient accord with this is: Having designed the stirring arrangements as seems best, select a speed that makes the known or estimated heating error safely negligible but little more than that. Afterwards if it should be found that the equalization is insufficient the remedy lies in improving the effectiveness of the circulation of the water; any allowable increase in speed will avail little in diminishing the total error.

Advantage of Temperature Integration. A less effective method of diminishing the need for equalization is to distribute the thermometer or thermometers throughout the calorimeter.[32] This is necessary for accurate aneroids, but has been little needed and little used in stirred calorimeters. It is easy with a thermel, but thermels are not much used; it requires a resistance thermometer of special construction,[33] and is out of the question for mercury thermometers.

Advantage of Change of Speed. Stirring is more needed at some times than others. Hence by appropriately slowing it down the heat and heat error can be considerably diminished. This has been discussed in the section on Timing.

[32] White, Walter P., *J. Am. Chem. Soc.*, **40**, 1862 (1918); Andrews, D. H., Lynn, G., and Johnston, J., *J. Am. Chem. Soc.*, **48**, 1277 (1926).
[33] Dickinson, H. C., and Osborne, N. S., *U. S. Bur. Standards Bull.* **12**, 33-37 (1915).

Advantageous Features in Design. It is hardly worth while to try to draw a sharp line between those features of calorimeter design which promote effectiveness, i.e., the amount of equalization for a given speed of flow, and those which promote efficiency, i.e., the amount of flow for a given heat production. Absence of dead spaces is the principal promoter of effectiveness. A rather long tube surrounding a propeller also promotes it. But if the end of the tube, where the flow turns, behaves like a "bend," which seems reasonable, a considerable portion of the heat is developed there. The bend is made sharper by coming too near the top or bottom of the water. An increase of effectiveness may thus be secured at the cost of efficiency. There appear to be no data directly applicable. The proper length of stirrer tubes is evidently one of the most important problems in stirrer design. A reasonable practical rule seems to be to be sure that the flow reaches the top and bottom of the water, but to take care that the tube is no longer than is necessary for that.

Ring stirrers, moving up and down, compare fairly well with propellers if the center of the calorimeter is not obstructed; the action is then somewhat like that of a frequently reversed propeller in a large central tube. Where the center of the calorimeter is blocked by a large object, as a combustion bomb, the ring stirrer, tho often used, is extraordinarily ineffective.[34] The stirring is almost confined to a flow around and thru the rings. The water cannot move along with them, because if it did it would have nowhere to go.

Efficiency, i.e., a high flow-heat ratio, is promoted by wide flow paths and a suitable propeller. I have given a calculation [35] indicating that where a propeller tube is already so small that the resistance to flow is mainly in it, a halving of its diameter increases the heat 16 times for the same flow, or is equivalent in its effect on the equalization error to increasing $K \sqrt[3]{16}$ times, or 2.5 fold.

Design of the Propeller. The velocity of flow past the surfaces of the propeller is somewhat greater than that anywhere else, but the amount of surface is so small that the propeller is probably a minority element in the heat production. A good design for it is worth considering, tho, even if far from vital. It is probably well enough to adopt the pitch and width of blade which have been found to give the best compromise between wetted surface and slip with larger pro-

[34] Mueller, E. F., *U. S. Bur. Standards Bull.* 11, 194 (1914). Richards, T. W., and Davis, H. S., *J. Am. Chem. Soc.*, 39, 350 (1917), report a case of ineffective stirring, but fail to identify the ring stirrer as responsible.

[35] *J. Am. Chem. Soc.*, 40, 387 (1918). Equation 23, below.

pellers. It seems foolish not to make the edges very sharp, since, whatever the gain may be, there is no difficulty or objection. But the "stream line" design, emphasized by some experimenters, is apparently fallacious as applied to calorimeters. The term usually means a screw, with the blades so curved that the forward component of motion is the same at all points on a radius, altho the circumferential velocity of course varies. This design is correct for a ship's propeller, moving thru water all of which is nearly at rest. But water moves thru a tube with least total friction when the motion at the wall is zero, and the velocity distribution across a diameter is parabolic. The stream-line propeller, however, tends to give maximum forward velocity next the tube wall, which causes excessive friction there, and consequent undue heat production. If the tip of the blade is flattened to diminish the velocity near the wall the ratio of circumferential to forward velocity is very unfavorable, so it is undoubtedly better to cut off this flattened tip, that is, to have the propeller smaller than the tube. The propeller will then actually drive a narrower column of water than the larger stream-line propeller would, and hence must turn faster. How short the propeller should be is uncertain. Table II (page 70) indicates that 60 per cent of the tube diameter is at least as advantageous as anything much larger.

The Stirring Speed and its Control. Altho, as already pointed out, a diminution of the heat for a given speed of stirring is relatively unimportant, since a slight decrease in the speed of stirring is equally effective, a large diminution may be valuable absolutely. And such can be obtained by using a governor to control the speed. If the constancy of the speed can be increased 27-fold, which may often be possible, the speed may be increased 3 times with no greater heating error. The resulting avoidance of error from uneven temperature is probably as great as by the use of a vacuum-walled vessel.

Stirring in Delicate or Accurate Measurements

The needed effectiveness of stirring varies as the proportionate accuracy desired. But the heat of stirring and its error will, for a given effectiveness, be no different whether the temperature rise is large or small and so will be larger in proportion with the small rise. Hence the stirring will, more than any other single feature, be most a problem when both delicacy and proportional accuracy are sought.

Increase of time increases the heat-of-stirring error almost proportionately, but scarcely affects the non-uniformity error, since a longer time involves a slower rise, with smaller temperature differences

at any one instant. This is also seen by noticing that the non-equalization error is practically a lag.

It follows that as the length of period increases the best compromise between effectiveness and low heating error shifts in the direction of slower speed.

The Stirring Needed

Two experimenters have estimated that a properly designed calorimeter with a propeller in a tube is stirred sufficiently for the highest precision when the temperature rise is 0.001° per minute. As one of the two I seem privileged to suggest that this statement should be revised. The heat is a very good property by which to define the stirring of a given calorimeter, for a considerable change in that accompanies a relatively small change in effectiveness. It is to the design, however, that most attention needs to be given, because any considerable change in that may alter the effectiveness very appreciably.

A heating of 0.001° per minute is, in fact, usually undesirably great for accurate work. If the temperature rise is 3° a precision of 0.1 per mille by **(4)** demands single errors less than 0.000 03°. This is 3 per mille of the heat in 10 minutes at 0.001° per minute. But a variation of 3 per mille in the heat corresponds to 1 per mille in the speed. Hence the governor must work constant to 1 per mille if the heating error is to be really negligible, as is desirable in view of the other errors which need attention when high precision is sought. On the other hand, if the heating is only 0.0001° per minute its error can readily be made negligible in nearly all cases, and the error, if any, from insufficient stirring will be little more than twice as great if the heat is diminished ten times by making the speed less. This is, after all, only an application of the rule already given that the heat of stirring should nearly always be made quite negligible. For 1 per mille precision the error of a heating of 0.001° per minute is evidently negligible ordinarily. Compare, however, page 184.

Tests of Stirring Efficiency. It is quite accurate enough, and very convenient, to treat the effect of stirring by considering the lags in the temperature of the calorimetric fluid, whose value is inversely as the equalization.[36]

This question was studied in a 3-liter calorimeter with central-tube stirrers. The arrangements were crude, calorimeter and jacket covers were of single sheet copper, 0.7 mm. thick, and altho the whole was in a constant-temperature box the very small heats of stirring were

[36] White, Walter P., *Phys. Rev.*, **31**, 575 (1910).

uncertain to 10 per cent and possibly a little more. The lags were equally uncertain for a different reason, a fluctuating irregularity of the temperature.[37] The calorimeter was 15 cm. in diameter, the tubes, 5 and 7.5, the propellers were 4 and 6.6 cm. long. The lag here given is that between the middle and bottom of the outside of the calorimeter. This was chosen because among all the differences between 6 points that were observed it followed most consistently the changes in stirring speed, and also because it was rather large. It is larger than the lag between any likely position of a thermometer and the mean external temperature. Table II gives some of the results.

TABLE II.—Efficiency of Calorimeter Stirring.

Propeller	Tube	Speed *RPM*	Temp. Rise *degrees per min.*	Lag *seconds*
small	small	500	0.0001	14
large	large	500	.001	4
large	large	250	.0001	8
small	large	500	.00006	5 or 6

The effect of change of speed with the large propeller is, within the errors of experiment, what would be expected.

Advantage of Large Tubes. If the speed given for the slow large propeller should be still further decreased till the lag of 8 seconds becomes the same, 14 seconds, as that of the small tube, the heats, now equal, would be in the ratio of $\left(\frac{14}{8}\right)^3$ or 5.4. That is, the efficiency was here multiplied more than 5 times by increasing the propeller tube diameter from one-third of the calorimeter diameter to half of it with a roughly corresponding change in the propeller. If equation 23 for the effect of tube diameter is applied, then since for the same flow the linear velocity is inversely proportional to the square of the tube diameter the ratio of the heats, V^3d, comes out $\left[\left(\frac{1}{2/3}\right)^2\right]^3 \times 2/3$, or $\left(\frac{3}{2}\right)^5$, or 7.6, instead of 5.4, as observed. A larger discrepancy in the same direction would not have been at all surprising.

Advantage of Small Propellers. The change of propeller in the large tube was from 88 per cent to 53 per cent of the tube diameter. If the stirring lags observed with each, 8 and 6 seconds, are supposed

[37] These fluctuations, tho undesirably large for this particular investigation, were not, in general, a defect. It is not necessary for the temperature readings that the temperature curve at any part of the fluid should be perfectly smooth, and the attempt to make it so would usually be very bad practice, since it would increase enormously the heat of stirring.

to be reduced to the same value, say, 8 seconds, by a change in speed, the heats become 0.0001° and 0.000 025°, or the short propeller gives only one-fourth of the heat for the same effectiveness. This is rather surprising, and confirmation is to be desired. Making generous allowance for possible experimental error it seems overwhelmingly probable that the gain by using small propellers, say 60 per cent of the diameter, will be well worth while.

The change to one-fourth the heat, is, of course, smaller when reckoned as effectiveness for the same heat; actually 59 per cent increase. But anything approaching this, so easily obtained, seems worth while.

It also seems to follow that when a propeller nearly fills a tube the production of heat near it is relatively very great. But this does not seem to cast any doubt on the conclusion above, that the design of the propeller, aside from its length, is not of first importance.

Conclusion as to Stirring Lag Error. In these experiments the lag, 5 seconds or so, obtained for a very wide stirring tube is still uncomfortably large, for a 10 per cent variation in it, as appears from the section on timing, would be very undesirable even if not serious in working for 0.1 per mille precision.

When tubes as wide as this cannot readily be used the situation is worse, and lesser degrees of precision, more often desirable, may be rendered uncertain. In such cases it seems that the rule should be to diminish the leakage modulus, K, either by using a vacuum-walled vessel, or by a convection shield. The adiabatic method also can be used to gain the same advantage.

Arrangement of the Stirring

A rather careful comparison, hitherto unpublished, showed that a ring stirrer in an unobstructed calorimeter was nearly but not quite as efficient as a propeller in a tube. The calorimeter was 15 cm. in diameter, the tube one-third of that, or 5 cm. Comparisons of other types of stirrer, such as the centrifugal, seem desirable.

A number of workers, in avoiding the very ineffective ring stirrer with combustion bombs, have put a propeller in a side tube. This is efficient enough if the tube is not too small. A very efficient calorimeter of that character was designed for me as early as 1906 by Dr. Arthur L. Day.[38] But the tube increases the complexity and cost of both calorimeter and jacket. The simpler cylindrical form, with propeller tube inside near one wall, and the bomb or other large object,

[38] White, Walter P., *Phys. Rev.* **31**, 671 (1910).

if any, unsymmetrically placed, is probably only negligibly inferior in effectiveness. Moreover, below the propeller the tube no longer needs to be circular in section. It can enlarge and flatten out, and be partly bounded by the calorimeter wall, thus avoiding dead water between wall and tube. A tight joining is not at all necessary; in fact, dead water near the tube may often well be avoided by making small openings.

The calorimeter with inclined internal stirring tube which I described in 1910 also proves on examination to yield no larger a space and no more effective stirring than a simple unsymmetrical tube can be made to give.

Size of Calorimeter in Relation to Stirring

The question of the best size is always involved in designing a calorimeter. Statements regarding the question frequently err by omitting important considerations. One of these considerations is the ease with which calorimeters of different size can be stirred. If we assume propeller stirring, as one of the best kinds, and one of the easiest to reason about, we may say that the stirring of different calorimeters of the same shape but different size is equivalent when the fluid makes a circuit in the same time. This means that the linear velocity of the fluid must be made proportional to the linear dimension of the calorimeter, which we may call n. The length and the diameter of the stirring path will also necessarily be proportional to n.

If the Engineer's approximate formula for friction of liquid in pipes, $\frac{lV^2}{c} = Pd$, where V is linear velocity; P, pressure; d, diameter; l, length; c, a constant for the pipe arrangement, is multiplied by Vd, the second member evidently becomes an expression for the work done on the stream, and therefore for the heat, so the other member,

$$\frac{V^3ld}{c} \tag{23}$$

also gives the heat. This formula is not supposed to be accurate; it is merely more probable than any other readily assignable. The factor l is especially doubtful, but if it is omitted the final result in the present case will not be much altered. The formula indicates that for equivalent temperature equalization the heat of stirring is proportional to n^4; really more than that, as some account should be taken of l.

The thermal leakage modulus, K, however, diminishes as the increase in n, and with it the need for temperature equalization diminishes,

Hence the stirring speed needed is not the equivalent one, but one $1/n$ as great as that, which reduces the heat by a factor $1/n^3$. The increase of heat, then, for equally satisfactory equalization is only that due to the factors dl, somewhere between n and n^2 times as great as in the smaller calorimeter. The resulting temperature change, however, on account of the n^3-fold size of the calorimeter, will be between n^2 and n times as *small*. But it will be n to n^2 times as large a part of the diminished total temperature rise, if the same amount of heat is measured in the larger calorimeter.

Section 8. The Thermal Leakiness, or Thermal Leakage Modulus, K

The thermal leakiness, K, is always found by actual measurement. It therefore, of itself, causes error only by failing to be constant. Its magnitude, however, determines the effect of errors in other quantities, particularly those from lags, and those in φ_x, which, by (2) is multiplied by K in finding the temperature loss η.

Elements of the Leakage

Thermal leakage is due to air conduction and convection, radiation, solid conduction, and evaporation. Evaporation is here treated as a separate effect.

Air conduction usually furnishes most of the leakage, tho least of the variation or error. It depends, according to well-known laws, on the conductivity of air and the geometry of the space around the calorimeter. It varies 0.0017 for each degree of change in mean temperature; that is, over 1 per cent between summer and winter.

Solid conduction is important in the glass necks of vacuum-jacketed vessels, and should be quite constant there. Conduction by supports, stirrer rods, or lead wires is usually of minor magnitude and easily calculated, except that it tends to vary with the excellence of contact between the conducting bodies and the calorimeter or jacket. Conduction thru the jacket along stirrer rods, thermometers or wires from the room atmosphere is largely independent of jacket temperature, and therefore not included in K. It is treated in the next section.

Radiation depends on the amount of calorimeter surface and on the character, including the cleanliness, of all the surfaces concerned, but is nearly or quite independent of distances. It increases 1 per cent per degree of mean temperature. On account of the smaller transfer by radiation the absolute amount of this variation is generally less than that of the air conduction, tho of the same order of magnitude.

General Character of Convection

Convection has been the cause of the greatest variations in K, and these can therefore be avoided by choosing such dimensions as will make convection negligible. This fundamental fact appears to have been first seen by Dickinson, who also showed that in horizontal heat flow thru narrow (1 cm.) vertical air spaces the currents flow up one

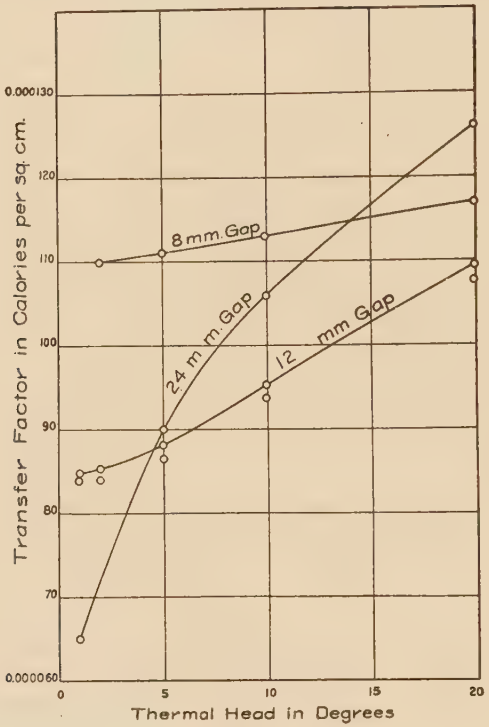

Fig. 7.—Heat transfer factor. Horizontal flow across vertical gaps 8 cm. high. The increase with thermal head is the convection effect.

side and down the other, with very little mixing. Convection in such spaces was investigated quantitatively by Dickinson and Van Dusen,[39] and also by me.[40] Dickinson and Van Dusen's research was much more extensive, but their results on convection were rather incidental and not all consistent. Hence my own presentation will be used here. It was made with special reference to calorimeters. As far as comparison is possible the results agree remarkably well with those of Dickinson and Van Dusen. I have given three rules: (1) The total convection

[39] "The Testing of Thermal Insulators," A. S. R. E. Journal, 3, 5 (1916).
[40] *J. Am. Chem. Soc.*, **40**, 382 (1918).

heat transfer is independent of height, that is, the transfer per sq. cm. is inversely proportional to height. The convection heat transfer factor is proportional (2) to the square of the temperature difference, and (3) to the cube of the gap thickness. These were derived theoretically, simply by applying the laws of stream line (non-turbulent) flow, taking the flow to be in two parallel sheets, as observed by Dickinson. The data obtained give numerical values for practical application, and also show that the rules apply rather poorly in some instances. "As the temperature difference increases there is a tendency for the transfer

TABLE III.—Heat Transfer, in the Usual C.G.S. Unit, i.e., Calories per Second per Degree of Thermal Head per Square Cm. of Flat Surface, 8 Cm. High, at 22.8° Mean Temperature.

Where two values are given they show the range among determinations with different methods of getting the temperature. It will be seen that the value of the convection is practically unaffected by this difference of method.

Thermal Head	8 Mm. Gap.		12 Mm. Gap.		24 Mm. Gap.	
	Total	Convection	Total	Convection	Total	Convection
0.99°			0.000 083 9 .000 084 8		0.000 065	
1.98°	0.000 109 .000 110		.000 084 0 .000 085 2	0.000 000 1 .000 000 4		
4.95°	.000 111	0.000 001	.000 086 6 .000 088 1	.000 002 7 .000 003 3	.000 090	over 0.000 025
9.89°	.000 112 .000 113	.000 003 .000 003	.000 093 7 .000 095 2	.000 010 .000 010	.000 106	over .000 040
19.76°	.000 116	.000 007	.000.107 7 .000 109 4	.000 024 .000 025	.000 126	over .000 060

to increase more rapidly than according to (2), which appears clearly in the 12 mm. gap results; with still more vigorous convection the increase with temperature grows less, as appears with the 12 mm. gap for 20° thermal head, and very markedly with 24 mm. These variations from the simple laws are probably due to the development of turbulence." Barry, working with an actual calorimeter, has since found for thermal heads under 1° convection effects far exceeding in magnitude those derivable for those heads from my results.[41] There are reasons for thinking that this convection is on the ends of the calorimeter, where the convection streams, moving up and down in close proximity to each other, are greatly restrained by turbulence as soon as a small value of the thermal head is exceeded. Absolutely, these

[41] *J. Am. Chem. Soc.*, 44, 927 (1922).

effects are very small. The final results for larger heads, taken from the original papers, are given here in Figure 7 and Table III.[42] The quantity given is not the total transfer, but this total divided by the thermal head. This, when multiplied by the area and divided by the heat capacity of the emitting body, has the dimensions of K. Of the top and bottom surfaces of the calorimeter, if these are horizontal, convection will take place on but one at any one time. For thin gaps the convection transfer for this one surface will be about twice as great per sq. cm. as for a vertical surface 7 cm. high. This is equivalent to assuming convection over both surfaces at the same rate per sq. cm. as for a 7 cm. vertical surface. Since the total convection effect for a vertical surface is nearly independent of height, the effect per unit area is inversely as the height.

Time Variation in the Thermal Leakage

Variation in K from one time to another is due to different causes and is of different import from variations during a single experiment. Day-to-day constancy is only needed for those methods which involve a previously known value of K, and the superior precision or speed which these methods may have is bought at the cost of whatever effort is necessary to keep K from changing. Such changes may be due to (a) changes of position, altering air or solid conduction (these are certainly preventable) or (b) soiling of the surfaces may increase radiation. In one case the maximum change producible by soiling a silver surface was found to be 36 per cent of K, but no change approaching this, which occurred in face of a nearly perfect radiator, would be likely to occur with both surfaces originally bright. (*See* page 176.) Probably one-tenth of the calorimeter surface would have to be well soiled to make a change of 1 per cent in K, and such an occurrence seems unlikely with careful experimenters. The variations of 1 to 2 per cent reported from some very careful work were perhaps due to conduction, of unappreciated magnitude, thru the jacket, or to the adsorptions treated by Barry.[43]

The temperature coefficient of the thermal conduction of air, and the similar effect with radiation, cause an unavoidable variation of K which should not be neglected in accurate work which assumes the constancy of K.

Change During the Experiment—Convection Error

The changes in K which come during a determination affect a far larger number of experiments, and may be much greater, than the

[42] *J. Am. Chem. Soc.*, 40, 382 (1918), *Phys. Rev.*, 10, 751 (1917).
[43] See Section 11, on evaporation.

changes from day to day, hence they are more important. They are mainly due to convection, as already said, and hence depend on the thermal head. They have been restricted by keeping the thermal head small, which ordinarily means working with a small temperature change. This often very undesirable limitation can be diminished by a design unfavorable to convection, and this can be secured by the aid of the convection data given above. Since the thinness of air gap which

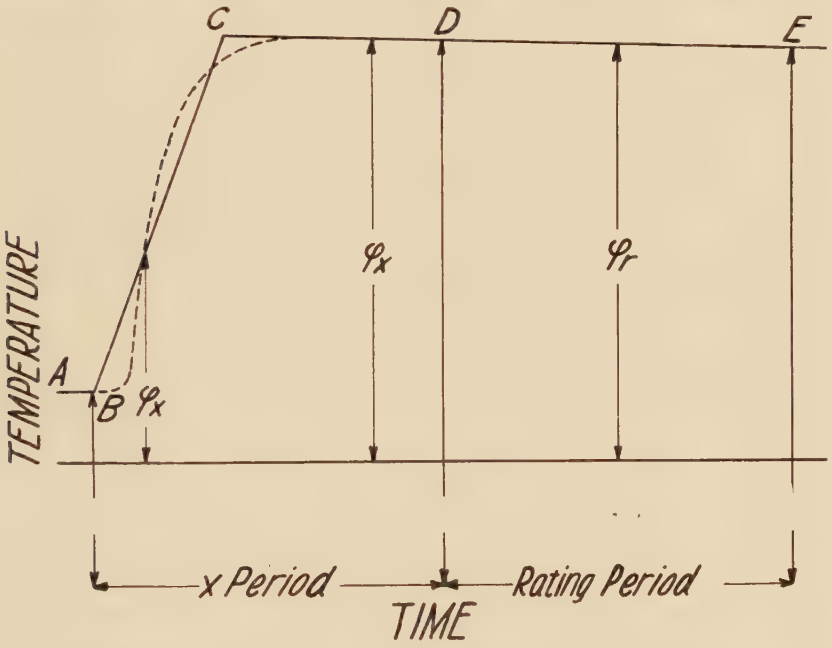

FIG. 8.—Temperature pattern diagram, accompanying the demonstration of the effect of convection.

makes convection small makes the total thermal leakage large, a balance must be struck between the opposing disadvantages. The convection and the error due to it increase about as the 3rd power of air gap thickness, while K diminishes at a less rate than the increase of the first power of gap thickness; this gives a case similar to that of the stirring error (pages 65 and 66). In this case, therefore, by analogy with that, the minimum total error will be obtained by making the convection error considerably smaller than the errors due to the magnitude of K. It will be simpler, however, to go beyond that, and make the convection error negligible for any thermal head that seems desirable. The final magnitude of K will seldom be materially different.

Value of the Convection Error. The final error due to variation in K may be found as follows:[44] For the temperature curve of the calorimeter during the X-period may be substituted, with more than close enough approximation, three straight lines, two horizontal and one inclined, *AB*, *BC* and *CD*, as in Figure 8.

Since we need to know only the approximate magnitude of the error it seems desirable to simplify the reasoning by treating the case where *AB* is at about the jacket temperature. Then φ_r will be about $\Delta\Theta$.

Since the thermal head along *CD* also is equal to $\Delta\Theta$ the thermal leakage rate corresponding to *CD* will be calculated, correctly, as equal to that observed in the rating-period, no matter what formula is used, or what may be the variability of *K*. The leakage corresponding to *AB* is negligible. That corresponding to *BC* remains. For $\Delta\Theta$ about 4° and a gap of 12 mm., the ranges of greatest interest, the convection factor increases as the square of the thermal head, as well as can be determined from my data. That is, the total thermal leakage rate may be put equal to $(K_o + a\varphi^2)\varphi T$, where *a* is a constant dependent mainly on the geometry of the air space. In the present case the observed value of *K* will therefore be $K_o + a(\Delta\Theta)^2$, and the computed leakage for *BC*, based on this computed value alone, will be $K\varphi T$, or

$$[K_o + a(\Delta\Theta)^2]\frac{\Delta\Theta}{2}T_B \qquad (24)$$

where T_B is the time covered by *BC*. But the real leakage will be $\int_o^{T_B} K\varphi dt$, and since, on account of the linear rise of temperature $\varphi = \frac{t\Delta\Theta}{T_B}$, this integral is:

$$\int_o^{T_B}\left[K_o + a\left(\frac{\Delta\Theta}{T_B}t\right)^2\right]\frac{\Delta\Theta t dt}{T_B} = \frac{K_o\Delta\Theta T_B{}^2}{2T_B} + \frac{a}{4}\frac{\Delta\Theta^3 T_B{}^4}{T_B{}^3} \qquad (25)$$

The error is the difference between (24) and (25) and this is

$$+ a(\Delta\Theta)^2 T_B\frac{\Delta\Theta}{4}. \qquad (26)$$

or one-fourth [45] of a leakage calculated for the main rise in temperature, the time occupied by it, and a value of *K* equal to the change in the real *K*, or $a(\Delta\Theta)^2$.

The error will be larger if the calorimeter is initially above the jacket temperature, or if instead of $K_o + a\varphi^2$ for the leakiness a higher

[44] White, Walter P., *Phys. Rev.* **31**, 554 (1910).

[45] In *J. Am. Chem. Soc.*, **40**, 384 (1918), I gave this number as 1/6. This value was taken from *Phys. Rev.*, **31**, 554 (1910), and was very nearly that observed in two actual calorimeters. It corresponds to the normal variation of convection. But the value 1/4, given here, is, as Table 3 shows, preferable for the range of gap thickness which is of most importance.

power of φ should be used. When the law of thermal leakage approaches $K_o + a\varphi$, or when the calorimeter temperature passes thru that of the jacket, the error will be smaller. A safe upper limit for the error is given by **(26)**.

This calculation gives only the order of magnitude of the error. An actual computation of it would usually necessitate treating BC as the curve that it really is.

Convection Error in the Microcephalous Method. In the microcephalous method (Section 3, § 5) the effective large temperature rise is that up to the jacket temperature, AC in Figure 4. This will usually be 0.8 $\Delta\Theta$ or more, its cube, 0.51 $(\Delta\Theta)^3$ or more. The convection error thus may be made only half as great by the use of this method. This advantage, apparently shown here for the first time, is the chief one which the method offers. It does not seem to compare with the disadvantages. To illustrate; suppose that convection was negligible in the first place, as it should be, and that instead of diminishing it the microcephalous method is used to keep it the same and diminish K, which can be done by increasing the gap thickness. The increase will be in the ratio $1 : \sqrt[3]{2}$ or 1 : 1.26, which, by Table IV, would cause less than a 20-per cent lessening of K and of the errors proportional to K.

The Convection Error and the Total Value of *K*. A calculation of the dimensions necessary to make convection negligible for an average calorimeter will serve fairly well for most cases and will furnish a model for others. It will also incidentally illustrate the computation of the total value of K. Suppose, then, a cylindrical calorimeter 11 cm. in diameter by 16 cm. high, holding 1460 cc. and having when filled a total heat capacity equal to 1500 grams of water. The area will be 740 sq. cm. The maximum temperature change for which provision will be made may be taken as 5°.

Barry [46] has given a rule for calculating the air conduction leakage for a calorimeter of practically the same size as the one supposed here. By this rule the results in Table IV are obtained. From Barry's results, also, 0.00027 should be added on account of radiation. This is done in column 5.

If the observed value is much larger than that derived by the present method some excessive and presumably remediable thermal leakage due to solid conduction, radiation, or evaporation is to be suspected. Two No. 18 copper wires, such as are sometimes used for electric heaters, would, if they ran directly across the gap, increase the leakage 30 per cent, and an iron stirrer shaft 2.5 mm. in diameter would

[46] *J. Am. Chem. Soc.*, **44**, 929 (1922).

TABLE IV.—Air-conduction Leakage for Different Gap Widths Around a Calorimeter 11 × 16 cm.

Gap cm.	Mean Radius cm.	Mean Height cm.	degrees per min. per degree of thermal head	
			K_C	K_T
1	6	17	0.00187	0.00214
2	6.5	18	0.00107	0.00134
3	7	19	0.00083	0.0011

K_C, part of K due to conduction alone. K_T, total, but with solid conduction and convection still neglected.

increase it 15 per cent. Nichrome has only one-fifth the conductivity of iron.

The error from change in K during a determination may next be estimated quantitatively. As the calorimeter is heated the jacket changes little, the absolute mean temperature of the intermediate space therefore changes half as much as the calorimeter. This, for a 5-degree rise, taking K as 0.002, gives from the temperature coefficient of air conductivity a change in K of $0.002 \times 0.0017 \times 5 \div 2$ or about 0.000 008 or 0.004 of K.

For a precision of 0.1 per mille, the convection error by (4) should not exceed 0.01 per mille of $\Delta\Theta$, and this, by (26), should equal $\frac{1}{4}(\delta K) T_B \Delta\Theta$. The maximum value of T_B may be taken as 2 min. for all ordinary cases. We thus have $0.000\,01\Delta\Theta = \frac{2}{4}\delta K \Delta\Theta$, whence δK should not be allowed to exceed 0.000 02, and since the change of 0.000 008, due to conduction, is inevitable, the change due to convection should not exceed 0.000 012. It may be well to add that while 0.000 012 is taken as more probable than 0.000 02, the uncertainty in the data almost amounts to the difference, and the difference cannot be important, since we are attempting to make the whole quantity negligible. The value of δK for 5° and 12 mm. may next be calculated. From Table III the heat transported per degree per sq. cm. by convection across a 12 mm. gap for 5° thermal head is about 0.000 003 2 calory per second, and 60 times that, or 0.000 19 calory, for a minute. This is for a surface 8 cm. high. For 16 cm. it is half as much per sq. cm., and this applies to the sides of the calorimeter, about 0.7 of the whole surface; for the horizontal ends, the convection, as already said, is that appropriate to a 7 cm. vertical wall, or $8/7 \times 0.000\,19$ per sq. cm.; the whole is very nearly 0.7 of 0.000 19, or 0.000 133. This

multiplied by the area, 740 sq. cm., is the total transport per degree per minute, and this divided by the heat capacity, 1500, is the change of temperature due to convection per degree of thermal head per minute when the thermal head is 5°. This is the change in K due to convection. It is 0.000 066, and should be as small as 0.000 012, as we have seen. The gap must therefore be made less than 12 mm. for the precision sought. The data of Table III indicate that the law for variation as the cube of the gap width holds very well for the values we are considering. Applying it, 12 mm. must be multiplied by the cube root of $12 \div 66$ or 0.567; the result, 6.8 mm., is probably the best distance for the conditions stated.

This value will change very slowly with change in the volume of the calorimeter.

Methods of Diminishing the Convection Error. This conclusion, as it stands, is rather unsatisfactory. For 0.1 per mille precision it is desirable to keep the leakage small, in order to avoid stirring difficulties, and a 7 mm. gap gives a rather large value of K, nearly 0.003. Moreover, with $K = 0.003$ the effective temperature coefficient of K is no longer 0.000 08 but 0.000 12, so that a further diminution of the convection is needed, with a further increase in K, and so on. If T_B is over 6 minutes the temperature coefficient alone will preclude the desired control of the error from variation in K, unless the gap can be made larger than 1 cm.

There are, however, a number of ways out.

1. The adiabatic method, the vacuum-walled calorimeter, and the convection shield all diminish convection greatly, and permit, or bring, a diminution in K which reduces the effect of the temperature coefficient, besides being of value otherwise.

2. If T_B is under 1 minute, as it will be, very nearly, in most cases, the allowable variation in K can be doubled. Since nearly half that was attributed to the temperature coefficient, doubling it will allow the convection effect to be about trebled, increasing the gap in the ratio $\sqrt[3]{3}$, or to 9.8 mm., which gives K about 0.002, and the temperature coefficient, therefore, no greater than was assumed.

3. If the temperature rise is made less, say 3°, the total convection error, proportional to $(\Delta\Theta)^3$, will be correspondingly lessened, and the relative error, or error divided by the rise itself, will be proportional to $(\Delta\Theta)^2$ or $\left(\frac{3}{5}\right)^2$ times as large. Hence the cube of the gap thickness can be increased in the same ratio. The gap thickness, for

the same precision, can therefore be made $\sqrt[3]{\left(\frac{5}{3}\right)^2}$ times as great as 6.8 mm. or 9.4 mm.

If the final precision is to be only 1 per mille, so that the convectional variation of K plus the temperature coefficient effect may be 10 times 0.000 02 for 2 minutes and 5°, the convectional variation may be nearly $0.000\,2 \div 0.000\,012$, or 16, times as large as that just treated, and the gap may be $\sqrt[3]{16}$, or over 2.5, times as thick, that is, 17 mm., with K very likely 0.0015. Similarly, it can be shown that for a precision of 0.3 per mille, probably the best yet reported, convection error is quite negligible for 2 minutes and 5° if the gap is 11 mm., which should make K equal to 0.002 for the calorimeter of Table IV.

If the convection error is allowed to exceed a little the other large errors, some increase in the gap is secured. But such a change violates the principle,[47] that where the decrease of one error involves the increase of another which varies as a higher power of the first, the second error should be kept negligible. The slight decrease in K would not be worth the cost.

Correcting the Convection Error. Another plan for dealing with the variation in K is to let it be appreciable and correct for it. A superior method of carrying this out was published in 1910 [48] in which advantage was taken of the fact that the variation of K due to thermal head is largely independent of the day-to-day variations. The variation with thermal head was determined once for all and then so treated that the determination and application of the daily value of K could be carried out much as if there were no such variation. The method is nearly as convenient as where K can be treated as constant, and gave almost unprecedented precision for intervals as great as 18°, with a very poorly designed jacket with which the variation of K was exceptionally large. The method is now needed only for very high precision, and one of the other schemes will often be preferred on account of other advantages; the reader is therefore referred to the original paper for details; but the method should not be forgotten, for it can completely suppress the convection error without complicating or restricting the apparatus or the choice of temperature interval.

Section 9. Leakage Through the Jacket [49]

The leads of electric thermometers or heaters, and half the wires of a thermel, are usually of good conducting copper, and usually

[47] Already stated in regard to heat of stirring, page 66.
[48] White, Walter P., *Phys. Rev.* **31**, 553 (1910).
[49] Reprinted from *J. Am. Chem. Soc.*, **40**, 1882 (1918).

run from the outside air through the jacket wall to the calorimeter, so that they may produce an effect which is due to the room temperature, and not taken account of in the thermal head measurement. Metal stirrer rods may also act in this way, but need not; in general the effect is one characterizing electric arrangements, and important only on account of the high precision which these make possible. It tends to behave as part of the constant rate w, just treated, but may cause error if the room temperature changes; it is an obstacle to operating with invariable leakage modulus, K, which involves a rate, V, proportional only to thermal head, φ; and it interferes more or less with the testing of K which is almost certain to be sometimes needed in careful calorimetric work. It therefore seems worth while to indicate how the order of magnitude of this effect can be determined.

THE FORMULA

The flow of heat along a wire is defined by the parameter $\mu = \sqrt{\varepsilon P/KA}$, where KA is the conductance, equal to conductivity, K, times area of cross section, A, and εP the emittance per cm., or emissivity, ε, times perimeter, P. For a wire running X cm. from an infinite body at temperature θ_o to another at θ_2 through a medium whose temperature may be taken as the zero, if the zero of coördinates is at the junction with the body at θ_o, the temperature at any point is, from a well-known equation:

$$\theta = (1/(e^{\mu X} - e^{-\mu X}))\{\theta_o(e^{\mu(X-x)} - e^{\mu(x-X)}) + \theta_2(e^{\mu x} - e^{-\mu x})\} \quad (27)$$

and the flow of heat at any point is KA times the derivative of this or

$$KA\,(d\theta/dx) = (KA\mu/(e^{\mu X} - e^{-\mu X}))\{-\theta_o(e^{\mu(X-x)} + e^{\mu(x-X)}) + \theta_2(e^{\mu x} + e^{-\mu x})\} \quad (28)$$

If 2 wires with different μ are in series between θ_o and θ_2, if we introduce the condition that at their junction point the flow is the same in each wire and solve for the temperature of that point, we find it to be:

$$\theta_i = \frac{2\mu KA\theta_o(e^{\nu Y} - e^{-\nu Y}) + 2\nu K'A'\theta_2\,(e^{\mu X} - e^{-\mu X})}{\mu KA(e^{\mu X} + e^{-\mu X})(e^{\nu Y} - e^{-\nu Y}) + \nu K'A'(e^{\nu Y} + e^{-\nu Y})(e^{\mu X} - e^{-\mu X})} \quad (29)$$

with the aid of which all temperatures along the compound conductor can be determined. ν, Y, K' and A' are used for μ, X, etc., of the second wire.

It will be sufficient to treat the case where θ_2 is at the same temperature as the air, that is, at zero, and where the wire is the same, but μ differs on account of the medium. The KA's then cancel out. The simplified Equation 29 then can conveniently be written:

$$\theta_i = 2\theta_o \cdot \frac{(e^{\nu Y} - e^{-\nu Y})/\nu}{(e^{\mu X} + e^{-\mu X})(e^{\nu Y} - e^{-\nu Y})/\nu + (e^{\nu Y} + e^{-\nu Y})(e^{\mu X} - e^{-\mu X}/\mu)} \quad (30)$$

and by substituting this in (28) for θ_2 or for θ_o with $\theta_2 = o$ the heat flow at any point can be found.

We may consider first a copper wire of 1 mm. (No. 18), for which $KA = 0.0075$, nearly. The radiation from a wire of this size, even with a black surface, is a small part of the conduction-convection loss in air, so that the character of the surface does not much matter. In the open air we may apply Langmuir's empirical rule, that the heat loss is equivalent to that passing to a perfect conductor through a 4 mm. layer of still air. This makes εP roughly 0.0002 c. g. s. and μ therefore 0.16. Where the wire goes through the jacket we may (1) suppose it to run between two copper plates, tangent at opposite ends of a diameter, separated by well-shellacked silk insulation 0.1 mm. thick, whose thermal insulation can be neglected in comparison with the air. A rather rough approximation based on the geometry of the air space then gives 0.0018 for εP, or 0.48 for ν. (2) If we suppose a flat strip of the same sectional area 0.1 mm. thick and therefore 8 mm. wide, insulated by mica of here negligible thermal resistance, but with equivalent air gap 0.2 mm. thick, due to imperfect fitting, εP is 0.004 and ν 0.73.

In determining the heat conducted to the calorimeter we may first find the temperature of the wire where it leaves the jacket for the outside air. It is easy to show by trial for the values of μ and ν just given that if the distance X in the air is not less than 20 cm., and in the jacket wall not less than 6 cm., either wire behaves regarding its initial temperature nearly enough as if it were infinitely long. For an infinite wire the equation is: $\theta = \theta_o\, e^{-\mu x}$ so that $d\theta/dX$ at the beginning of the wire ($x = o$) is $-\mu\theta_o$. Hence, by putting the initial flow equal in both wires we find that the difference of temperature between wire and jacket is $\mu/(\mu + \nu)$ times the jacket-air difference, or about $0.16/(0.16 + 0.48)$, or one-fourth of it, in the worst case here supposed, and nearly one-fifth in the other, where a strip continues the wire. In calculating the effect of this initial temperature we may preferably take the calorimeter at the temperature of the jacket, since the effect of any difference between them will count as part of the ordinary thermal leakage of the calorimeter; it is only the effect of the room outside that we are now seeking. Equation (28) therefore applies, modified by use of (30), and yields the following results in different cases.

RESULTS

Heat flowing to the calorimeter in 10 minutes per degree difference of air and jacket:

Through 6 cm. No. 18 wire between plates	+ 2 cm. air inside.....	0.03 cal.
6 cm. No. 18 wire between plates	+ 6 cm. air inside.....	0.012
12 cm. No. 18 wire between plates	+ 2 cm. air inside.....	0.0017
6 cm. No. 18 wire	air only.....	0.33
6 cm. flat strip	+ 2 cm. air inside.....	0.0061

In the last two cases the initial temperature on the wire was not taken at one-fourth the room-jacket difference, but one-half or one-fifth of it, respectively. The strip is supposed to be continued by a wire in the outer air. Some of the heat lost through the inner air gap goes to the calorimeter, but this is a minor effect.

It is clear that under proper conditions a pair of No. 18 copper wires will not conduct enough heat through a jacket to cause appreciable error, but the thermal contact with the jacket may easily be worse than that here supposed. A flat strip rolled around a copper rod or tube, with shellacked silk between, gives a better thermal contact than that assumed here, and gives it very easily.

Application to Thermometers. In 1918 I pointed out that the numerical values given at the top of this page indicated that nearly a calory per degree of thermal head might be conducted down the stem of a Dickinson-Mueller calorimetric resistance thermometer in ten minutes. A change to much slenderer lead wires has now greatly reduced this possible conduction. Anything like approaching an exact calculation is difficult, but there is some indication of 0.06 calory for 6 cm. of contact between the case and the jacket. This is generally negligible. The 50 wires of a 24-junction thermel usually have, all told, less than half the thermal conductance of a single No. 18 wire, and of course their heat emitting power per cm. of length is very much greater. Hence it appears that a thermel can safely be used under any but the most exceptional conditions, if the precaution be taken of running it 6 cm. or more in approximate contact with the jacket. This conclusion has been directly supported by experiments in this laboratory.[50] A 24-couple thermel inclosed in a glass tube 5 mm. in diameter, which made a barely easy fit in a brass tube 6 cm. long, ran from a submarine, vacuum-jacketed calorimeter to an ice bath. The thermal head was zero, the stirring too slow to produce appreciable change of temperature. In one case, with the room 6° colder, the temperature read constant to 0.000 05° for 4 hours, changing 0.000 2° in the next two hours. Another trial showed a fluctuation of 0.000 15° in an hour, though without final change. A more certain

[50] Due to Mr. Earle R. Edson.

indication, perhaps, is offered by the result when a 96-junction thermel was also inserted in the same calorimeter, for the value of $K\mu$ with this was 6 or more times that with the smaller one, and effects from other causes were consequently less likely to falsify the results. The change was now 0.000 1° (0.1 calory) in 10 minutes per degree of air to bath temperature difference, which corresponds to less than 0.02 calory with the smaller thermel. (When this larger thermel was itself used for reading to 0.000 012° in a calorimeter holding only 200 cc. it was covered with a carefully fitted "straddler," or sheet copper cover dipping in the jacket water, thus virtually bringing the whole thermel inside the jacket.)

Section 10. Lags

Calorimetric lags occur when any portion of the system reaches its temperature later than the body on which calculation is based. They result from the imperfection of temperature equalization; hence there is a lag in the stirred liquid and lags in all the bodies into which heat flows by conduction. When depending on conduction they obey very simple laws, and hence can be accurately treated. This is fortunate, since it is almost impossible to measure most of them directly.

Imperfect temperature equalization may also produce steady temperature differences, and most parts of the calorimeter show these as well as lags. The logical distinction between the two, however, is simple and clear: lags are proportional to the rate of temperature change; the other differences to the thermal head.

Thermometer Lag

Thermometric lag furnishes a good introduction to the whole subject of lags proper. Let L be the lag, defined by the equation

$$(\theta - u) = L\frac{du}{dt} \tag{31}$$

where θ is the temperature of the calorimeter, u, of the thermometer. L is then also the time interval between the reaching of a given temperature by a *uniformly* changing calorimeter and by the thermometer, and can also be found for constant $\theta, = \theta_o$ by means of the equation:

$$u = \theta_o + (u_o - \theta_o)e^{-\frac{t}{L}} \tag{32}$$

obtained by solving (31) with u_o as the value of u for $t = 0$.

At the ends of a determination, that is, when the only cause of temperature change in a calorimeter is thermal leakage, the rate, V, is $K\varphi$, and the temperature difference of thermometer and calorimeter is

$LK\varphi$, to a close approximation. This $LK\varphi$, taken alone, constitutes an error in the temperature determination; the net error of the terminal measurements is the difference of the errors of the two, or $LK(\varphi_r - \varphi_a)$, and this, *for constant jacket temperature,* is

$$LK\Delta\Theta. \qquad \text{(L2)}$$

This formula was given in 1903 by Jaeger and von Steinwehr, who proposed to apply it as a correction in actual work. T. W. Richards independently proposed a similar procedure. With $K = 0.003$ and L 10 seconds, or one-sixth minute, as it might be for a mercury thermometer, the correction is 0.0005 or 0.5 per mille. Thermometric lag is thus almost inappreciable in work of 1 per mille precision, and this is true of most lags.

Negligibility of Thermometer Lag. In 1908 I showed that tho formula **L2** is correct, the proposed application made of it was not, since there is another thermometer lag effect—that during the X-period —which opposes and neutralizes the one in the end temperatures. There is of course a temperature difference due to lag during the rapid rise. This is multiplied by the small quantity K in getting the leakage effect, η, so it was not thought to be important. But the fact was overlooked that the lag temperature difference in the X-period did not yet contain K as a factor, while the other already did, so the quantity in the X-period to be multiplied by K was very much larger. Actually, the mean rate V_x is $\frac{\Delta\Theta}{T_x}$, the mean resulting temperature error, $-L\frac{\Delta\Theta}{T_x}$. The multipliers of this are K and T_x, so the error is $-LK\Delta\Theta$, equal and opposite to **(L2)**. Here some small quantities have been neglected, but when all these are counted the final error is rigorously zero, if the environing temperature and the lag itself are constant. This was proved by me in 1910 and confirmed by Harper.[51] The quantity at issue, a small part of the small lag effect, seems too unimportant for a third presentation.

Evidently an appreciable thermometric lag will cancel out in the way just described only when the same thermometer is used to indicate the calorimeter temperature throughout.[52]

When the time of the temperature rise is inferred from the manipulation, that is usually equivalent to measuring it with a different thermometer. In such cases there will be a resultant lag effect, as in the experimental demonstration of that effect in 1905 by Theodore W.

[51] Harper, D. R., 3rd, "Thermometric Lag," *U. S. Bur. Standards Bull.*, **8**, 702 (1912). The treatment of the lag of a Beckmann thermometer in this paper is noteworthy.
[52] White, Walter P., *Phys. Rev.*, **31**, 565 (1910).

Richards, Lawrence J. Henderson and George S. Forbes. The same is true, as Dr. Richards reminds me, if the temperature loss is taken as equal to the change in the rating period, or when no regard at all is paid to it. In such relatively crude methods the lag effect, from $0.0004\Delta\Theta$ to $0.001\Delta\Theta$, is usually of minor importance, but nevertheless need not be overlooked. It is quite satisfactorily eliminated if experimental calibration is used, or if an easily determined correction is applied. It is shown (page 42) that in taking the temperature loss equal to the rating period loss, i.e., $\varphi_x = \varphi_r$, the error, for $K = 0.002$, $T = 10$ min., may be less than 0.001. The thermometer lag effect is then important. But if the legitimacy of assuming $\varphi_x = \varphi_r$ is proved experimentally, the regular thermometer will generally be used, and the automatic elimination of its lag effect will be a part of the result. A correction for thermometer lag will then produce an error.

General Law of Lag

The thermometer is probably the only body connected with the calorimeter which has equal and compensating lag effects in X-period and rating period. Other lags are of portions of the calorimeter or of bodies near it; those that are a matter of surface temperature affect only the temperature loss, η; the effect of others is mainly confined to the temperature change, $\Delta\Theta$. Each of these effects is, in non-adiabatic work, like each of the thermometer lag effects, approximately [53] equal to $LK\Delta\Theta$, where L is any lag, except that the lag in minutes must be multiplied by the fractional part, f, of total surface or heat capacity which is constituted by the lagging body or material in question, giving

$$fLK\Delta\Theta \qquad \text{(L2,b)}$$

for the effect as a fraction of the temperature rise, $\Delta\Theta$. Such effects, tho seldom compensating each other, have the following very important property: Since K is constant, the lag effect, as long as L remains unaltered, varies only with $\Delta\Theta'$, being independent of the length of the X-period or the form of the temperature-rise curve. Hence it is practically equivalent to a small addition to the heat capacity, since this also is multiplied by $\Delta\Theta'$. It is therefore completely eliminated in an experimental calibration. When the calorimeter is calibrated, it is calibrated, lag effects and all. These effects will change only if L or K changes, or if the jacket temperature is not constant.

All Constant Lags Negligible with Experimental Calibration. That these partial lag effects are proportional to $\Delta\Theta'$, the corrected temperature rise, may need a word of explanation, since they have

[53] White, Walter P., *Phys. Rev.*, **31**, 568 (1910); *J. Am. Chem. Soc.*, **40**, 1860 (1918).

usually been given as proportional to the *observed* rise, $\Delta\Theta$. When the final *temperature* of some part of the cooling calorimeter is read too low on account of lag, so that the interval $\Delta\Theta$ is in error by the small fraction $-fLK$, as already shown, the final *rate* reading will be made low in the same proportion, and so, accordingly, will be the calculated temperature loss, η, hence the total lag effect will be $-fLK(\Delta\Theta+\eta)$ or [54] $-fLK\Delta\Theta'$.

With the lag of the surface the matter is more complicated. The surface leads the thermometer during simple cooling, and the magnitude of the lag is likely to be different according as the heat is coming from some hot body to all the fluid, or from all the fluid to the surface, as it does in the rating period. Calling the two values of the lag L_1 and L_2, and inserting them in the simplified equation, $V_r\frac{\varphi_x}{\varphi_r}T$, for the temperature loss, we get for the true loss, if φ_x and φ_r are the observed values and for equal periods, considering that both lags are present in the X-period,

$$V_r\frac{\varphi_x-L_1\frac{\Delta\Theta'}{T}+L_2\frac{\eta}{T}}{\varphi_r+L_2\frac{\eta}{T}\frac{\varphi_r}{\varphi_x}}T \qquad \textbf{(L3b)}$$

which may be more evident if it is also written in the equivalent form:

$$V_r\frac{\varphi_x-L_1\frac{\Delta\Theta'}{T}+L_2\frac{K\varphi_xT}{T}}{\varphi_r+L_2\frac{K\varphi_rT}{T}}T$$

All that has been done is to put as the temperature equivalent of each lag the lag multiplied by the average rate of the corresponding temperature, in one case,[55] $\frac{\Delta\Theta'}{T}$, in the other, $\frac{\eta}{T}$, equal to $\frac{K\varphi_xT}{T}$, and in the rating period $\frac{K\varphi_rT}{T}$, equal to $\frac{\eta}{T}\frac{\varphi_r}{\varphi_x}$.

The $+$ signs in **(L3b)** are consistent with the fact that L_2 is a lead, and therefore naturally of negative sign among lags. If L_2 is taken simply as a number, then, since the thermal head is less than the thermometer indicates, both terms will be negative. But the conclusions drawn will be the same.

[54] I have not treated this particular $fLK\eta$ effect before. But if we notice that the temperature difference due to lag is always proportional to thermal head in the rating period, the lagging part may be considered as one whose final temperatures are a little higher than those of the rest of the calorimeter, which makes it equivalent to one of equal temperature but larger heat capacity. This is the same result as by the other treatment.

[55] *See* paragraph 2, p. 90.

If $L_1\Delta\Theta/T$ is small, the last terms in numerator and denominator bear the same ratio as the numerator and denominator themselves, and therefore may be omitted without altering the value of the fraction. The numerator thus becomes simply $\varphi_x - \frac{L_1}{T}\Delta\Theta'$. The effect of the X-period, or surface lag, then, is like that of other lags, very nearly proportional to $\Delta\Theta'$, not $\Delta\Theta$, and therefore equivalent to a modification of the heat capacity of the calorimeter. If L_1 is 10″, $L_1\Delta\Theta'/T$ will be $\frac{\Delta\Theta'}{30}$ or less, and the error incurred by omitting the η terms corresponds to $\frac{1}{30}$ of the very, very small $LKT\eta$, or $LK^2T\Delta\Theta$ term.

In actual fact, the temperature does not rise to $\Delta\Theta'$. But the heat flow corresponding to that rise does actually take place, and as a result of it the temperature gradient from thermometer to surface is, at a time when the calorimeter temperature is about stationary, larger than it is later, when the temperature is falling and the only heat flow is that which supplies the heat lost from the surface. If the flow were in solids, and therefore strictly in accordance with Fourier's Equation, the superposition of these two flows and lags would be complete, and Equation **L2b** (page 87) and its corollaries could be taken rigorously. But a stirring lag cannot be taken as having quite the same regularity and constancy as a lag where conduction in solids is concerned.

The whole subject of these $fLK\eta$ terms can now be stated more completely than has been done hitherto. There are three classes of these effects. (1) A capacity lag in the rating period affects alike the temperature rise and, thru the rate, the temperature loss. Its effect is therefore proportional to $\Delta\Theta + \eta$, that is, to $\Delta\Theta'$. (2) The surface lead due to thermal leakage, L_2 of **(L3b)**, cancels between X-period and rating period. (3) The lag in getting the heat to the surface in the X-period, L_1 of **(L3b)**, has an effect which is practically proportional to the total heat supplied, or to $\Delta\Theta'$, tho this is partly concealed in the temperature curve.

I called attention to these $fLK\eta$ effects in 1910 and again in 1918, and suggested that the errors they cause can be avoided by using the adiabatic method wherever η is large. It had not then been shown that the $LK\eta$ effects make the total lag effect more nearly proportional to $\Delta\Theta'$ than it would be without them. The conclusion that these effects are a reason for using the adiabatic method has now lost most of its force.

Ordinarily these effects are exceedingly small. In one case, where

a calorimeter rim lagged 10 seconds and formed one-tenth of the surface its *main* lag effect was less than $0.000\,05\Delta\Theta$; and the $fLK\eta$ surface effect under 10 per million for a period an hour long.

Best Place for the Thermometer. The temperature difference between thermometer and calorimeter surface which constitutes the X-period lag is lessened as the thermometer is put nearer the surface. Indeed, a thermometer rather near a colder part of it might be at the average temperature of the whole. With such placing, tho, the irregularity of the thermometer would be likely to more than neutralize the advantage of having its mean temperature near the mean of the surface. This is because the coldest parts of the calorimeter surface are those near the feeblest circulation. Proximity to the surface even where the circulation is vigorous tends to subject the thermometer to short irregular fluctuations during cooling, tho not to any worse ones during rapid heating. Hence as long as the thermometer shows a steady rate during the rating period it is not too near the surface. The nearer it can be got without unsteadiness the better. It does not seem important to make any elaborate experiments to determine the distance, however.

This lag should be distinguished from the thermometer lag. In fact, it causes the thermometer to lead the surface. It is, strictly, a lag of the surface behind the water surrounding the thermometer, with which the thermometer lag will be combined, but which is due to different causes, and is likely to vary in a different way.

Effect of Size on Lag Error

In the expression for the proportionate lag effect, namely, $\frac{fLK\Delta\Theta}{\Delta\Theta}$, or fLK, fK is the only multiplier of L. Hence an increase in size of the calorimeter, which usually makes both f and K smaller, diminishes the effect of any given lag and tends to diminish whatever error there may be. But K usually varies very slowly with the volume of the calorimeter, so this consideration is of minor importance, except with aneroid calorimeters. This does not apply to the stirring lag.

Lag Error with Jacket Temperature Change

It has been repeatedly said, in this book and elsewhere, that the compensation or elimination of lag effects in non-adiabatic work fails if the jacket temperature changes. The size of the resulting error is easily found. The temperature effect of the lag is lag $\times$ rate, or LV, or $LK\varphi$, and this changes by about $LK\Delta\Theta$ during the X-period, as a

result of the temperature rise, $\Delta\Theta$. A change, ε, in environing temperature changes φ by ε, which therefore tends to cause an error of $LK\varepsilon$. This is the value for the thermometer lag, which affects the whole calorimeter; for a partial lag the fractional factor f must be added, giving $fLK\varepsilon$. But the effect of environing temperature change on the determination of the leakage effect, η, by **(15)** is $T_xK\varepsilon$. Any conditions which make this disappear will make the corresponding lag error still more negligible.

This reasoning is sufficient wherever constancy of jacket temperature is relied on to prevent error in η. If the jacket temperature is observed to prevent such error, and is consequently allowed to vary, the resulting lag error remains. But in this case there is usually a process of compensation which makes the error exceedingly small. Change in jacket temperature practically always results from difference of temperature, either between jacket and room, or between jacket and calorimeter. And either of these temperature differences rather tends to persist, and hence to make the jacket rate nearly constant for moderate time intervals. And the effect on lag of a constant rate largely cancels. For if the effect $fLK\varepsilon$ during the X-period is positive, and increases the temperature rise $\Theta_3 - \Theta_2$, during the rating period it will be the same, and will diminish the temperature fall $\Theta_3 - \Theta_4$. Since in finding η the $\Theta_3 - \Theta_4$ is normally multiplied by a factor nearly equal to unity (Footnote 6, Chapter II), the only error remaining is a higher-order effect.

Taking the thermal leakiness of the jacket to the room as 0.0025, T as 10 minutes, K as 0.003, the lag as $\frac{1}{6}$ minute, and calling the thermal head of the jacket φ_c, $LK\varepsilon$ is $\frac{1}{6} \times 0.003 \times (10 \times 0.025 \times \varphi_c)$, or $0.000\,012\ \varphi_c$. And since this effect largely cancels, then unless φ_c is ten times $\Delta\Theta$, or changes in ten minutes by an amount greater than $\Delta\Theta$, the lag error due to it will surely be negligible.

Lag of External Shields or Packings

The lag of layers of metal, air, or other material surrounding the calorimeter demands for adequate representation more complicated expressions than those already presented. A discussion [56] of these is repeated next, with some minor changes. A special numbering of the equations is given, so as to preserve that of the original publication without duplicating any numbers used above in this book. The rest of the present section deals with the lags and other heat-flow effects in bodies more or less external to the calorimeter. It treats, first, external

[56] White, Walter P., *J. Am. Chem. Soc.*, **40**, 1863-69 (1918).

"radiation" or convection shields, used to diminish heat loss, where a knowledge of the magnitude of the lag effect is desirable, and second, larger or less definite masses, where it is enough to know the general laws of the effects.

Let us first suppose, between a calorimeter and its complete jacket, a thin metal shield, between whose different portions there are no temperature differences great enough to prevent the average temperature of the shield from being treated as a single uniform temperature.

Let u be the temperature of the shield, θ, of the calorimeter, C, of the calorimeter chamber, i.e., the jacket.

K_1 be the leakage modulus of the shield with respect to the calorimeter, that is, the value the modulus would have if the leakage took place only to the calorimeter.

K_2 that of the shield with respect to the chamber.

K_3 that of the calorimeter with respect to the shield.

K_4 that of the calorimeter with respect to the chamber directly.

(This evidently supposes that the shield does not inclose the calorimeter completely.)

The meaning of these *partial leakage moduli* is defined by the following equations:

$$du/dt = K_1(\theta - u) + K_2(C - u) \qquad \textbf{(L4)}$$

$$d\theta/dt = K_3(u - \theta) + K_4(C - \theta) \qquad \textbf{(L5)}$$

Evidently K_1 and K_3 have to do with the same transfer of heat, and their ratio is that of the heat capacities of shield and calorimeter, respectively. That is, if H is heat capacity of the calorimeter, h of the shield,

$$h/H = K_3/K_1$$

From **(L4)** follows readily, by integration:

$$\int_x [K_1\theta + K_2C - (K_1 + K_2)u]dt = \Delta u \qquad \textbf{(L6)}$$

where $\int_x$ means the integral over the X-period.

Approximate Solutions. The essential facts regarding external lag will perhaps be more readily seen if the demonstration is first outlined in an approximate form sufficient for most practical purposes, after which the results of closer approximation may be indicated. The final temperature rate of the calorimeter, that is, the change during the rating periods, which is very slow compared to that in the X-period, may therefore be first taken as zero. We then have for that final condition:

$K_2(u - C) = K_1(\theta - u)$, that is, the same amount of heat leaves the shield as enters it. Solving for u we get:

$$u_r = \frac{K_1\theta + K_2C}{K_1 + K_2}, \text{ whence } \Delta u = \frac{K_1\Delta\theta + K_2\Delta C}{K_1 + K_2} \qquad \text{(L7)}$$

or

$$(\theta - u)_r = \frac{K_2}{K_1 + K_2}(\theta - C)_r \qquad \text{(L8)}$$

But Δu in **(L6)**, referring to the ends of the X-period, refers to the rating period conditions which hold for **(L7)** and **(L8)**, hence substituting the value of Δu from **(L7)** in **(L6)** we get:

$$\int_x [K_1\theta + K_2C - (K_1 + K_2)u]dt = \frac{K_1\Delta\theta + K_2\Delta C}{K_1 + K_2} \qquad \text{(L9)}$$

Now the thermal leakage from the calorimeter during the X-period is, really:

$$K_3\int_x (\theta - u)_x dt + K_4\int (\theta - C)_x dt \qquad \text{(L10)}$$

But in getting it we ordinarily measure, not $\theta - u$ but $\theta - C$ during the X-period, and instead of getting K_3 and K_4 we measure the leakage during the rating periods, dividing it also by the thermal head $(\theta - C)$. That is, we actually find:

$$\int (\theta - C)_x dt \, \frac{K_3(\theta - u)r + K_4(\theta - C)_r}{(\theta - C)_r} \qquad \text{(L11)}$$

The difference between **(L10)** and **(L11)** is the error due to the shield and its lag. **(L8)** and **(L9)** enable us to find it. First, however, it is evident that the coefficient of K_4 is the same in both equations, that is, the lag of the shield does not interfere with a correct determination of that part of the leakage which flows by the shield. If **(L10)** is subtracted from **(L11)** to find the lag effect the terms in K_4 cancel, and therefore contribute nothing to that effect. Hence we may omit them.

Formula **L11**, the observed leakage effect, thus abbreviated, becomes, by **(L8)**,

$$\int (\theta - C)_x dt \, \frac{K_3K_2}{K_1 + K_2} \qquad \text{(L12)}$$

If we now modify the integral in **(L9)** by adding and subtracting $K_2\theta$ and uniting the θ-terms with those in C and u, and finally multiply the whole by $K_3/(K_1 + K_2)$, we get:

$$K_3\int (\theta - u)_x dt - K_3\int \frac{K_2(\theta - C)_x dt}{K_1 + K_2} = K_3\left[\frac{K_1\Delta\theta + K_2\Delta C}{(K_1 + K_2)^2}\right]_r \qquad \text{(L13)}$$

Here the first term is the true leakage of **(L10)**, the second is the leakage as found, or **(L12)**, and their difference is the second member, which is the desired lag effect.

It will be convenient to eliminate K_3 by means of the relation $h/H = K_3/K_1$. We thus have the lag effect as:

$$\frac{h}{H}\frac{K_1^2\Delta\theta + K_1K_2\Delta C}{(K_1+K_2)^2} \qquad \textbf{(L14)}$$

in terms of the relative heat capacity of shield and calorimeter and of leakage moduli pertaining to the shield. We have seen that lag effects have generally been simplified in discussion by taking ΔC as strictly zero. *Unless this is true in practice it is* incorrect *to treat the lag as a constant modification of the heat capacity.* The adiabatic method, however, also deserves consideration, in which $\Delta C = \Delta\theta$. For these two cases, **(L14)** evidently becomes:

$$\text{Constant jacket, } \frac{h}{H}\left(\frac{K_1}{K_1+K_2}\right)^2\Delta\theta \qquad \textbf{(L15)}$$

$$\text{Adiabatic method, } \frac{h}{H}\left(\frac{K_1}{K_1+K_2}\right)\Delta\theta \qquad \textbf{(L16)}$$

Interpretation. A word may be in order as to the physical meaning of these expressions. The expression **(L16)** is strictly not a lag effect at all, but the heat lost to the shield. If K_1 is very large that means that the shield is very near the calorimeter. The expression then reduces practically to $h\Delta\theta/H$; that is, the capacity of the shield is directly added. If the shield is about half-way out, so that $K_1 = K_2$, **(L16)** becomes $h\Delta\theta/2H$, in accordance with the evident fact that half of the heat gained by the shield now comes from the calorimeter. Expression **(L15)** is the resultant of the heat given to the shield (in this case $hK_1\Delta\theta/H(K_1+K_2)$, all of it from the calorimeter) and a true lag effect in the leakage from the shield. The calorimeter gives less heat to the jacket through the shield while it is heating up the shield. The lag effect alone, that is, $-hK_1K_2\Delta\theta/H(K_1+K_2)$,[2] can easily be obtained directly by a calculation similar to that already employed. Although it does not look so at first sight, this is equivalent to the $LK\Delta\theta$ X-period lag listed above, for $1/(K_1+K_2) = L$, the lag of the shield, $K_1\Delta\theta/(K_1+K_2)$ is the temperature change of the shield, K_2 is the leakage modulus by which its integrated temperature must be multiplied to get the leakage to the jacket, and hK_2/H is this modulus in terms of the effect on the calorimeter. Dickinson [57] has also treated

[57] Dickinson, H. C., *U. S. Bur. Standards Bull.* **11**, 204 (1914).

the convection shield mathematically, with results which at first sight appear quite different from those given here. The difference, however, is easily explained, and comes from the fact that, wishing merely to illustrate possible errors in existing procedure, he found approximate methods sufficient. Thus his much larger value for the effective heat capacity of the shield is precisely the one obtained here when the effect of lag on that capacity is disregarded. A simple derivation of **(L15)** is given in Section 24.

More Rigorous Solution. To obtain a more rigorous treatment of the external lag effect we need to solve **(L4)** and **(L5)** to get the relations of u, θ, and C for the rating period. The solution, carried out by standard methods, shows that for constant C u-C and θ-c are each equal to the sum of two exponentials, one of which has essentially the time-rate of decay of the shield temperature, and is to be omitted, since we have not reached a "final" value till this has become negligible. The other exponential is essentially the cooling rate of the calorimeter. The expression for u-C and that for θ-c have the same exponential. Taking the ratio of the coefficients of this exponential we have

$$\frac{u-C}{\theta-C}=\frac{K_1}{K_1+K_2-K_3-K_4+K_3K_n} \qquad \textbf{(L17)}$$

where K_n is a series of terms containing increasing powers of $K_3/(K_1+K_2)$, or something similar, which may be neglected if K_3 is small compared to K_1 or K_2.

Equation **L7** now changes from

$$u_r=\frac{K_1\theta+K_2C}{K_1+K_2} \text{ to } u_r=\frac{K_1\theta+(K_2-K_3-K_4)C}{K_1+K_2-K_3-K_4}$$

that is, with the calorimeter cooling, the shield, on account of its own lag, does not take quite the same intermediate temperature as it would with the calorimeter constant. Carrying the calculation through for the changed value of **(L7)** we get for the lag effect, instead of **(L14)**:

$$\frac{h}{H}\left\{\frac{K_1^2\Delta\theta+K_1(K_2-K_3-K_4)\Delta C+K_1^2(K_3+K_4)\int_x(\theta-C)\,dt}{(K_1+K_2-K_3-K_4)(K_1+K_2)}\right\} \qquad \textbf{(L18)}$$

Here the difference between the first two terms and **(L14)** is not important, since as far as they are concerned we still have a constant multiplier of $\Delta\theta$ if ΔC is zero, or else get the same value as **(L16)** for the adiabatic method. But the value of the integral term is dependent on the way in which the temperature rises, and corresponds closely to the small $LK\eta$ or $LK^2\varphi_x T_x$ term in the other lag effects which have been considered.

Lag of Layers or Packing. With the preceding demonstration in mind it is easy to solve the problem of a very large number of shields, and this is of practical importance, since it enables us to treat the case of a thick insulating *layer*, by considering that as made up of a large number of shields packed together.

Suppose, then, a number of shields, S_2, S_4, S_6, ... $S_p - 2$, whose heat capacities are h_2, h_4, etc. Let their temperatures be u_2, u_4, etc., with $u_o = \theta$, the temperature of the calorimeter, and $u_p = C$, that of the chamber. Let K'_1, K'_3, etc., be the thermal leakage moduli between each two adjacent pairs of shields, expressed as *calories* transferred per degree of temperature difference. The ordinary leakage modulus for the nth shield is then $K'_{n\pm1}/h_n$.

The only assumptions are that the h's and K's are constant. This evidently includes the assumption that Fourier's equation for heat conductivity holds.

Let us first treat the terminal or rating period values of the u's and C as constant, and let us take ΔC, the change in the jacket, as either $= 0$ or $= \Delta\theta$, since we have seen that only in these two cases do we get a definite result practically.

Now for any shield, say the 4th, we have, as in **(L6)**:

$$\Delta u_4 = \frac{K'_3}{h_4}\int_x (u_2 - u_4)\,dt - \frac{K'_5}{h_4}\int_x (u_4 - u_6)\,dt \qquad \textbf{(L19)}$$

Whence:

$$K'_3 \int_x (u_2 - u_4)\,dt - K'_5 \int_x (u_4 - u_6)\,dt = h_4 \Delta u_4 \qquad \textbf{(L20)}$$

By combining these equations one after the other we can get expressions connecting $\int(\theta - u_2)$ and $\int(u_4 - u_6)$, $\int(\theta - u_2)$ and $\int(u_6 - u_8)$, etc., from which we can, by addition, get a relation between $\int(\theta - u_2)$ and $\int(\theta - C)$. The only multipliers needed are the K's, which are constants. The various Δu's will appear in this final equation multiplied by terms composed of these constant K's. But each Δu is, as in **(L6)**, the difference of initial and final values, here provisionally assumed constant. Moreover, in these terminal states the temperature distribution, depending only on the distribution of insulating and conducting matter, is always the same, that is, each final Δu is always the same fraction of $\Delta\theta$, and the final term containing all the Δu's may therefore be written $f(K, h)\Delta\theta$, where $f(K, h)$ is constant as long as the apparatus undergoes no change. Our relation between $\theta - u_2$ and $\theta - C$ may therefore be written:

$$K''\int_x (\theta - u_2)\,dt - f_1(K, h)\Delta\theta = K'''\int_x (\theta - C)\,dt, \qquad \textbf{(L21)}$$

where K'' and K''' are more or less complex combinations of the constant K's.

For the final temperature distribution we may evidently write:

$$K'_3(u_2 - u_4)_r = K'_5(u_4 - u_6)_r, \text{ etc.,} \qquad \textbf{(L22)}$$

since the heat flowing into each shield is now equal to that flowing out. But this series corresponds exactly to the series of integrals **(L19)** with the heat capacity terms left out. Hence if we find a value for the relation of $(\theta - u_2)_r$ to $(\theta - C)_r$ it will have the same coefficients made up of K's as the corresponding result for the integrals. Hence we may write, referring to **(L21)**:

$$\frac{K'''\int_x(\theta - u_2)dt - f_1(K,h)\Delta\theta}{K''\int_x(\theta - C)dt} = 1 = \frac{K'''(\theta - u_2)_r}{K''(\theta - C)_r} \qquad \textbf{(L23)}$$

Whence, multiplying by $K_1K''\int_x(\theta - C)dt/K'''$, where K_1 is the modulus of the calorimeter with respect to the shield next to it:

$$K_1\int_x(\theta - u_2)dt = K_1\int_x(\theta - C)dt\left(\frac{\theta - u_2}{\theta - C}\right)_r + f_2(K,h)\Delta\theta \qquad \textbf{(L24)}$$

Here the first term is the true thermal leakage; the second is the computed leakage, derived from observations of $(\theta - C)_x$, of $(\theta - C)_r$, and of the actual leakage $K_1(\theta - u_2)_r$; and $f_2(K,h)\Delta\theta$ is the lag effect, corresponding to **(L15)**, but unknown as to its exact value.

The problem can be still further generalized. Instead of a series of shields we may take any constant distribution of matter whatever, with the heat liable to flow in any direction. Equations **L19** and **L20** will then be replaced by something far more complex, but what is essential for the present demonstration will remain, namely, that the only difference there is between the law of heat flow or temperature distribution in the X-period and in the rating period will be due to the heat capacity of the material, and will have an effect which is a constant multiple of $\Delta\theta$. Equation **L24**, therefore, will still hold, though with $\theta - u_2$ now as a mean. A layer of heat insulating material, therefore, or any other layer, has a constant lag effect, like a single shield, a fact which many experimenters have probably suspected, though it does not appear to have been proved before, and is only true with certain restrictions.

Equation **L24** is a generalization of **(L13)**, and like it, neglects the effect of any change in the calorimeter during the rating period. Analogy indicates that a more rigorous solution would correspond to **(L18)**, and contain a small term in $\int(\theta - C)dt$, like the $LK\eta$ term of other lags.

Duration of Shield Lag. It should of course be borne in mind that the above demonstrations regarding external lag hold only where

the X-period is made so long that the exponential which is characteristic of the lagging material sinks to a negligible value. For a bright silver shield 0.1 mm. thick one cm. from calorimeter and jacket the temperature has gone about

99 per cent of the way to equilibrium in 3 minutes **(L25)**

while if 0.5 mm. thick the shield would still be about

10 per cent away after 8 minutes. **(L26)**

The long time required for equilibrium will generally constitute a decisive objection to the use of thick layers of external material or thick covers, except where these are of good conducting metal, in close thermal contact with either jacket or calorimeter.

Section 11. Evaporation

Among the various things affecting a calorimeter, evaporation is the most complicated, and usually the most irregularly variable. In general, it may take the forms of: (1) distillation over to the wall of the calorimeter chamber, a process varying with the thermal head, tho not proportional to it, and varying also with the absolute temperature; (2) an increase in the saturation of the air in the calorimeter chamber, beginning immediately after any temperature rise, but accomplished in a time which is generally unknown; (3) a very uncertain distillation from chamber wall to the calorimeter when the calorimeter is colder and any moisture has been left in the chamber; (4) when the jacket is open, a distillation into the room which persists for a thermal head of zero, and is also variable with thermal head and absolute temperature; (5) evaporation of water adsorbed on the calorimeter surface, or adsorption upon it.

Amount of Distillation

In one case [58] the steady distillation to the chamber wall from an open calorimeter was found to be about 0.01 calory per minute per sq. cm. for 1° of thermal head. The corresponding temperature effect will usually add about three-tenths more to the thermal leakage. It involves 1 mg. per *hour* per sq. cm. per degree, but, being affected by convection, bears no definite relation to thermal head. It is not proportional to thermal head even in the absence of convection, as several writers have pointed out. With poorly-conducting jacket covers, the

[58] Observed by Earle R. Edson· reported in *J. Am. Chem. Soc.*, 40, 381 (1918).

distillation doubtless falls off somewhat as the cover warms up, thus adding to the error which may come from the falling off in the evaporation rate as the air is saturated.

Saturation of the Air in Adiabatic Working

If the amount of air in the calorimeter chamber is put at 700 cc., a fair value for a liter calorimeter, and the change in the vapor pressure of water at 1 mm. per degree, then the change in vapor content per degree is about 0.7 mg. Since the heat of vaporization of water at ordinary temperatures is around 600, or 0.6 calory per mg., the heat required for the evaporation which maintains saturation during a temperature rise is about 0.4 calory per degree, or around 0.4 per mille of the total heat. This applies to adiabatic working, where both walls of the air space, and therefore all the air in it, are changed by the full amount of the temperature rise.

This saturation effect, like a number of others, tends to cancel when the calorimeter is calibrated experimentally. Only its variations then remain as sources of error. These variations, however, are relatively large, and need scrutiny whenever the small effect itself is not easily negligible. A temperature coefficient close to 5 per cent per degree of absolute temperature, which applies to the distillation also, is slight and easily taken account of. But the time required to accomplish the saturation is of great importance. A very slow process would be running at about the same rate during the rating period as in the experimental period, and hence would have its effect eliminated entirely by the temperature loss calculation, as the thermal leakage has. A very rapid process would be practically complete in the experimental period, and would exert a maximum influence, whether that period were lengthened or not. But a process extending to a varying degree into the rating period would cause a doubled variation, first by the absence of some of its effect from the experimental period and second by the addition, in the temperature loss calculation, of that part of it which ran into the rating period. A change in the length of the periods might thus alter the effective heat capacity of the calorimeter. The rate of saturation is readily calculated by the method which Andrews and Johnston [59] based on the work of Williamson and Adams. The saturation may be taken as complete at the calorimeter rim, with one-dimensional diffusion occurring downward for a distance, a, about 2 cm. greater than the height of the calorimeter. Then the deficiency of saturation remaining after periods of 5, 10, and 20 minutes will be:

[59] Andrews, D. H., and Johnston, J., *J. Am. Chem. Soc.*, **46**, 642 (1924).

TABLE V.—Deficiency of Saturation in the Calorimeter Chamber After Different Time Intervals.

a Height + 2 cm.	t = 300 seconds	t = 600 seconds	t = 1200 seconds
12	0.223	0.062	0.005
15	.356	.156	.030
17	.426	.225	.063
18	.458	.259	.083
20	.510	.321	.128

A value of 12 cm. for a corresponds to a calorimeter only 10 cm. high. For such a calorimeter, with a five-minute period, and for calorimeters much higher at any period ordinarily used, any considerable change in the length of period may cause an error comparable to the total heat expended in changing the saturation. With $a = 17$, for instance, 57 per cent of the saturation change is accomplished in 5 minutes, which is 37 per cent more than the amount, 20 per cent, occurring in the next 5 minutes, on which the calculation of temperature loss would be based. But in the first 10 minutes 78 per cent of the total change is accomplished, or 62 per cent more than the amount in the next 10 minutes. Hence if an adiabatic calorimeter 14 or more cm. high is calibrated with either 5 or 10 minute periods, an error of 62-37 per cent, or 25 per cent, of the heat needed to change saturation is likely to result from working with the other period length, unless a correction is applied.

ADSORPTION EFFECTS

These amounts of vapor, moreover, are almost insignificant compared to the 20 to 30 mg. which, according to Barry,[60] may be adsorbed on the surface of an extraordinarily clean calorimeter, and also on the inner jacket wall. How these adsorptions are affected by changes of temperature and vapor concentration is not known, but it is known that they may begin when the calorimeter is put in place, and continue at a varying rate all thru the time of an ordinary experiment. The various possibilities which they threaten, exceeding the uncertainties of the air saturation, discussed in the preceding paragraphs, conspire with these to deprive the adiabatic method of the advantage it was long supposed to have—that of avoiding evaporation error with open calorimeters.

Barry's results show, however, an adsorption rate for a dry surface in saturated air little exceeding 3 calories in 10 minutes, and, what is

[60] *J. Am. Chem. Soc.*, **44**, 931 (1922).

much more important, only varying 0.4 calory in 10 minutes. Adsorption on the larger surface exposed by the jacket would of course be greater, but on the other hand 0.4 calory is a maximum, likely seldom to be reached unless special pains were taken to that end. Hence if a rating period is run, and for short experiments, the error from adsorption with an open calorimeter is not likely to exceed a few tenths of a calory. This conclusion, however, and those on the next six pages generally, should not be accepted without comparing the late addition on page 107.

Inclosure by a Sleeve Against Evaporation in Adiabatic Working

Three remedies for the difficulty are: (1) Simplest in principle and most certain, to prevent evaporation altogether. (2) To run a sleeve (paper and mica have been used) from the rim of the calorimeter up to the ceiling of the calorimeter chamber. Saturation of the space immediately above the calorimeter will be so rapid that no error from its delay need be feared, and adsorption error can be avoided by so manipulating the temperatures that all the walls of this space are moist before the beginning of the experiment. The thermal leakiness, K, of the calorimeter, and consequently errors from failure to know the value of φ, the thermal head, will be increased 30 per cent or so.

It is evident that the sleeve continuing the calorimeter upward is, in its relation to evaporation, closely analogous to a cover, and needs to be equally tight. To really keep it so seems likely, in daily work, to be more troublesome and uncertain than the manipulation of a tight calorimeter cover. Its only real advantage seems to be in avoiding the seal thru the cover with a propeller stirrer.

(3) The similar inclosure of a space immediately above the water, reaching to the jacket, is especially easy with vacuum-walled glass calorimeters, since the most convenient jacket cover with them is very often a plate put across the mouth of the glass vessel.

Dangers of Saturated Air

One serious disadvantage of a vacuum-walled vessel so treated, and of the completely saturated air so generally permitted above adiabatic calorimeters, is the impairing of the insulation of electric heater leads. The remedy seems to demand fragile glass inclosing tubes, water-tight joints, an undesirable shortening of the leads—in short, a good deal of inconvenience, and considerable chance of failures.

With non-adiabatic calorimeters and the restricted evaporation

recommended below for them, the trouble is far less. The only place for condensation is on the jacket surface, and there the equipotential shield [61] and paraffining of the surface seem to offer a complete and easy remedy.

Saturation and Inclosure in Non-Adiabatic Calorimetry

With ordinary calorimeters the amount of saturation must be less than with adiabatic, because vapor in the air space is continually condensing on the cool jacket surface; but both amount and speed of saturation are more uncertain, because the saturation is affected by convection, which varies very greatly with the thermal head. Convection undoubtedly tends to quicken the saturation, but rough calculations based on the probable speed of the air currents, as indicated by the thermal effect of convection, lead to the conclusion that no real benefit is derived in this way.

Imperfect Closing Effective in Non-Adiabatic Work. Simple and imperfect restriction of evaporation, however, is far more effective in ordinary calorimetry. This is because the air-gap is surrounded by the cooler jacket, which can, by condensation, remove vapor from the space much more rapidly than diffusion thru a narrow chink can supply it. Hence (1) almost the entire resistance to diffusion is situated in the narrow passage, and (2) the concentration of vapor outside that never varies far from the value corresponding to the jacket temperature; such slight variations as may occur, since they affect directly only a small part of the diffusion resistance, can be made to have a negligible effect on the now small total evaporation. Quantitative data are greatly to be desired. Meanwhile approximate guidance can perhaps be derived from the observed fact that the thermal effect of the evaporation across a centimeter cube is of the order of 0.01 calory per minute for 1°. The effect, then, may be put as

$$0.01\ \varphi A/l \text{ calory per minute,} \qquad (33)$$

where A is the section of the throttled path, and l its length. Dividing this by 1000 φ gives for a calorimeter of 1000 gm. heat capacity the portion of K which is due to evaporation. If A is 1 sq. cm., l, 1 cm., this is 0.000 01, which in 1 minute would produce an effect constituting a tolerable single error for 0.1 per mille precision. (*See* Equation **4.**) If the variation, and therefore the error, is as great as one-tenth, the diffusion path, therefore, might ordinarily be 1 sq. cm. in section without great detriment. The diffusion rate $0.01\varphi A/l$ is moreover an

[61] White, Walter P., *Phys. Rev.* **31**, 687 (1910); *J. Am. Chem. Soc.*, **36**, 2015 (1914); *see also* Figure 9.

overestimate, since convection must have aided the distillation in Mr. Edson's experiments.

The notion just presented, of throttled evaporation as very constant in rate, tho simple enough, seems to be new. It makes the task of suitably controlling evaporation seem much easier than might be inferred from most previous discussions—from my own at any rate—and leaves less excuse than ever for failure to accomplish that.

Floating Cover. The light floating cover,[62] for instance, whose simplicity and negligible lag are very attractive in many situations, now appears far more valuable, since it can often be used, even for 0.1 per mille precision, without the messy oil sealing hitherto considered necessary. A cover 2 cm. high, with a clearance of two-thirds mm., would offer the diffusion path which has just been shown to be usually safe. The floating cover seems to offer a good way, apparently long needed, of providing the vacuum-walled calorimeter with two covers, one in contact with the calorimeter water, the other with the jacket circulation.

Nearly Tight Covers. More convenient in some ways, and still more effective in restricting evaporation, the fairly tight cover over the top of the calorimeter also gains by the conclusion that oil sealing is usually unnecessary, even in work of high precision. Such covers should overlap, like the cover of a baking powder can, in order that the diffusion path may have some length, as well as narrowness.[63] These covers may consist of overlapping parts; they may thus be more readily opened or closed while structures running into the calorimeter are left undisturbed. Shutters, also, to close openings quickly, may be freely used, if there is enough overlap. To minimize lag effects, they should be as thin as possible. The top cover itself should have possible lag effects diminished by being directly connected with water thru good conducting projections. Even then the lag will be greater than that of a floating cover, but error will very seldom result.

Adsorption in Non-Adiabatic Calorimetry

The adsorption discovered by Barry does not seem likely to have any detrimental effect during the X-period and after in ordinary calorimetry. Condensation of any sort is not probable on a calorimeter wall several degrees warmer than the jacket wall in close proximity to it. Barry's surfaces lost their adsorbed water in ordinary air, not especially dried, whence it appears very unlikely indeed that they

[62] White, Walter P., *Phys. Rev.*, **25**, 137 (1907); *Am. J. Sci.*, **28**, 339 (1909).
[63] Overlap may also be desirable in a sleeve inclosure (page 102). This fact has some influence on the relative convenience of sleeves and calorimeter covers.

would take up any unless the air was close to saturation at the calorimeter temperature. There would be, then, with a calorimeter nearly closed, merely the slight evaporation already discussed. The final destination of the vapor is largely immaterial as long as it does not recondense on the calorimeter.

With small thermal heads, however, some of the escaping vapors might, as far as is now known, be adsorbed on the calorimeter, returning their latent heat to it in a way which is at present likely to be uncertain, and therefore to be a possible source of error. Before the X-period also there might be adsorption on the calorimeter surface of vapor whose subsequent partial evaporation would be uncertain.

Remedies for Adsorption in Non-Adiabatic Work. These difficulties seem avoidable in one of several ways. (1) By keeping a low saturation in the air space thru the use of drying material. This is an experimental complication, but the complication is chargeable rather to the adsorption than to the presence of a slight evaporation. Even where the attempt is made to restrict evaporation completely, the drying material is desirable for the best work, especially in damp weather. For the best results the air-drying material should of course be removed before the beginning of the experimental period. (2) By taking advantage of the fact that adsorption is large only when the air is near saturation, and avoiding this condition by dissolving some salt, or other suitable substance, directly in the calorimeter water. This method, inadmissible in some cases, might be only a trifling complication in others. It may be necessarily present anyway. The extent of its usefulness cannot well be judged till more is known as to the adsorption. (3) If the gap and calorimeter are dry at first the adsorbed layers must be made up from the vapor which escapes from the calorimeter after it is put in its chamber and before the temperature rise begins. It has just been shown, in connection with Equation 33, that for a floating cover without oil the vapor escaping is likely to correspond to 0.1 calory per degree of thermal head in 10 minutes. If the evaporation into a partly saturated space, where the difference in vapor pressure is likely to be around 10 mm. of mercury, is taken as equal to that for 10° of thermal head the total involves about 1 calory. Some of this would go to increasing the saturation of the air, and certainly more than half of the rest, if deposited at all, would be on the jacket, where it does no harm. As soon as the air got near enough to saturation to cause much adsorption the vaporization rate would fall to a small fraction of the value just derived. Hence it is very generous to suppose that the amount of adsorbed water, capable of causing an error by

re-evaporating, might correspond to 0.3 calory in 10 minutes. This is negligible for 1 per mille precision with $\Delta\Theta$ equal to 3° or more. With a "nearly tight" cover the showing is still more favorable, tho the calorimeter, as far as our present knowledge indicates, cannot safely be left in its chamber for a long time before the experiment, unless drying material is used. If drying material is still desirable, it is more because the chamber-wall surface may not be dry at the start than from any doubt as to the above estimate of error. As far as we know now it is probably important to take care that the calorimeter chamber wall is not liable to adsorb vapor from the jacket water, as already pointed out in Section 4. It seems probable that further knowledge may considerably lessen the above estimate, but of course there is no assurance of this at present. (4) By using a vacuum-walled calorimeter. The thing needed is prevention of condensation on the outside of the calorimeter, and this is evidently secured. A wide-mouthed, more convenient vessel could be used, since the object is not to diminish K, and all diminution that came would be "velvet." Incidentally, the convection error would be almost obliterated. The real trouble is the possibility of change in the adsorption on the upper side of the cover. Barry found the maximum adsorption effect to be 0.035 calory per sq. cm., which would be 1.7 cal., or say 0.0017°, with a wide-mouthed liter vessel. Not all of that would enter as error, by any means, and the prospect of high precision with slight evaporation is by no means hopeless. But it seems impossible at present to be sure of anything except tight closing, or drying material with nearly tight closing. Further data are most urgently needed.

Organic Liquids for Diminishing Evaporation

High-boiling organic liquids, as aniline and kerosene, have been used instead of water, for various reasons, one of which is the restriction of evaporation.[64] The weight of such liquids vaporized under given conditions may be less, and the latent heat is less than one-eighth that of water. The most important question, however, is evidently that of adsorption with such liquids. Of that we appear to know nothing. The chance that such liquids may help the evaporation problem seems good, however.

Other Features of Organic Liquids. Organic liquids, on account of their much smaller volume specific heat, give a greater temperature rise in the same calorimeter, which diminishes the leading calorimetric error, the accidental rise-and-rate error (see page 61). But for the same reason the leakage modulus, K, is larger with them. Using a smaller

[64] Andrews, D. H., Lynn, G., and Johnston, J., *J. Am. Chem. Soc.*, **48**, 1277 (1926).

calorimeter with water is therefore often a better way to get a large rise. A still greater disadvantage is the small heat-equalizing power, due to small heat capacity and even more to small conductivity, which increases the non-equalization error (pages 65 and 66).

The electric insulating power of the organic liquids is often advantageous, both in allowing bare heaters and bare thermels to be used, and because surfaces wet with their vapor, as in adiabatic work, do not leak. Compare also Section 22.

Further Conclusions about Adsorption

As this book finally goes to press Dr. Barry and Mr. Elliott P. Barrett informally report confirmation by another method of Dr. Barry's earlier results. By a simple gravimetric method, avoiding an error probably present in my 1910 results, I find for *sheet* nickel about 0.007 mg. per sq. cm., and for *sheet* gold less than 0.004, against Barry's 0.06 for plated gold. These sheet metal results are higher than the 0.001 mg. found by McHaffie and Lenher [65] for platinum, but all the results as a whole support the position [66] that the adsorption is primarily a capillary phenomenon, and also indicate that sheet metal, being less porous than plated, has less adsorption. Calorimetric observations on the copper block of page 166 indicated that the adsorption on its nickel-plated surface was comparable with that found by Barry for gold plating, and also that the adsorption extended to lower pressures than for sheet metal. But these results require confirmation on less heterogeneous surfaces. It appeared very clearly, however, that of the long time reported by Barry for adsorption much was due to diffusion of the vapor. Re-evaporation to the adjacent jacket surface, therefore, is relatively rapid.

Hence it follows, supposing that complete absence of adsorption is unattainable: (1) With sheet metal instead of ordinary plated surfaces the initial adsorption rate would not be much less, but would die away faster. That might be a disadvantage in adiabatic work, unless the plan was to get complete adsorption before the experimental period begins. This would occur very much sooner with sheet metal. (2) In non-adiabatic work with nearly-tight covers the adsorption, by (3), page 105, depends almost entirely on the amount of previous evaporation. But it should take over an hour to evaporate the 5 or 6 mg. usually required to bring half-saturated air to the point where adsorption begins. Hence adsorption would often be negligible, while on damp days,

[65] McHaffie, R., and Lenher, S., *J. Chem. Soc.*, **127**, 1559 (1925); Lenher, *ibid.*, **128**, 1785 (1926); **129**, 272 (1927).

[66] Frazer, J. C. W., Patrick, W. A., and Smith, H. E., *J. Phys. Chem.*, **31**, 897 (1927).

or with too free evaporation from the jacket, air-drying would be needed. The only difference a plated surface would make is that this point would possibly be reached at a very few millimeters lower vapor pressure. Where air pressure is on tap, a stream of dried air, running in a tube thru the jacket water to the lower part of the calorimeter chamber, may be more convenient than drying material in the chamber. (3) As a rule, where there is a convection shield and also evaporation from the calorimeter, some of the vapor may condense on the inside of the shield, whether there is adsorption or not. Hence the shield and evaporation have in this book been treated as incompatible (e.g., page 186). But with a nearly-tight cover, and air even half dry, the condensation should not begin for an hour, hence the shield can be used with no more complication of apparatus than is often needed without it.

A satisfactory gravimetric experiment indicates that the thermal effect of the adsorption of kerosene on sheet gold will usually be under 10 parts per million. But confirmation is desirable.

Practical Conclusions as to Evaporation

The best methods of dealing with evaporation thus appear to be:

For Highest Precision. *a.* In both adiabatic and non-adiabatic calorimetry; suppression of evaporation, as by oil-sealed covers, preferably with drying material in the air gap somewhere, especially in damp weather. *b.* In non-adiabatic work, nearly tight sealing, with removable air-drying material sometimes essential, tho often not. *c.* In adiabatic work, a *tight* sleeve, sealing in the space above the calorimeter. Danger to electric insulation in the damp space must be looked out for.

For Less Precision. Most calorimetry of modern precision, and some of better grade, has been done with free evaporation. Success in such cases must have been somewhat dependent on constant conditions. The increase in precision caused by controlling evaporation better does not seem to have ever been reported. Quantitative predictions seem difficult. The experimenter wishing to get along with free evaporation apparently must be guided by the experience reported for similar systems, or by his own.

Section 12. Chief Sources of Error

From the discussion so far the principal sources of error, in the order of their importance, are seen to be:

1. The rise and rate temperature measurements.
2. Stirring or non-equalization.
3. Evaporation.

4. Convection.
5. Following a rapid temperature rise.

The others are merely things that must not be altogether overlooked.

Number 2 is generally likely to be smaller than 3 or 4, but is harder to be certain about. The technic which *avoids* 3 is clear enough, but the best way of *dealing with it* is often not so, at present.

Number 4 can be estimated rather closely, with a choice of methods for eliminating it.

Number 5 is troublesome only in special cases.

1. The final effect of the error in the principal temperature measurements depends on the ratio of temperature rise to thermometric precision, and can be diminished by increasing either. It has been suggested (page 33) that the probable error of one of these important temperature measurements should be not much more than 0.075 of the "allowable" error. This allowable error is one which can be allowed and still leave the precision a fairly certain matter; it is the error which would probably occur in the mean of pairs of duplicate determinations one time in 300. If the probable error of a single observation is, as suggested, 0.03 scale division, the scale division must be as small as $0.075 \div 0.03$, or about 2.5 times the allowable error. For 1 per mille precision, or an allowable error of $0.001\Delta\Theta$, the scale division would be $2.5 \times 0.001\Delta\Theta$, or $0.0025\Delta\Theta$ and $\Delta\Theta$, the temperature rise, would have to be $\frac{1}{0.0025}$, or 400, scale divisions. This is 4°, for a thermometer divided in hundredths. Similarly for different final precision, or where difficulty in reading makes the probable single error more than 0.03 scale division.

If the final precision is defined as equal to the probable final error or average agreement, then (as shown on page 32), it is counted 3 times as good. A final precision of 1 per mille, reckoned in this way, ought to be reached with a temperature rise of less than 2° with a thermometer divided in 0.01°.

2. A well-designed calorimeter may have a mean stirring lag as great as 10 seconds, or one-sixth minute (*see* Table II). Since this is a lag, its effect is eliminated by experimental calibration in so far as the lag is constant, but is eliminated less perfectly than that of most other lags, which are due to conduction, and hence are more constant. If this lag is supposed to vary 2 per cent, and if K, the thermal leakiness of the calorimeter, is equal to 0.002, the resulting error will be, by **(L2)** (page 87) $\frac{1}{6} \times 0.002 \times 0.02$, or 0.000 007 times the tem-

perature rise, $\Delta\Theta$. This is 0.07 times the allowable final error in 0.1 per mille precision, and is therefore, by the preceding paragraph, a satisfactory, tho not a specially small value where such precision is sought. But 2 per cent is, as far as is now known, a high degree of constancy to expect from a stirring lag. Hence it will generally be desirable, for this very high precision, to diminish the stirring lag error thru using a very large propeller tube or thru diminishing K by means of a convection shield, a vacuum wall, or by using the adiabatic method. The value of K attainable by any of these methods, however, will seldom be as small as one-third of the ordinary. Hence stirring lag seems to join temperature measurement, in constituting the most serious obstacles to further extensions of precision.

For 1 per mille precision the stirring speed and consequently the equalization can be doubled, since the stirring heat and its error will then only be 8 times as great. Even without this increase the constancy of the lag now needs to be only 20 per cent. Hence there is no need of lessening K, tho that is now easier, and may be desirable for other reasons.

3. Evaporation proper can always be eliminated by a vapor-tight cover, and adsorption error also, tho it seems much safer to use drying material as well. In adiabatic work error from both evaporation and adsorption can be avoided by restricting evaporation to a small, sealed space, whose walls are all damp. This can be done by a tight sleeve or with a vacuum-walled vessel. In non-adiabatic work drying material plus a nearly tight cover seems quite sufficient. Free evaporation from the top of an ordinary calorimeter increases the thermal leakiness, K, by about 0.0006, and little will generally be known as to the probable constancy of this part of K.

4. In working to 0.1 per mille precision convection may often be one of the larger errors, even tho, in order to limit it, the air gap is reduced to the undesirably small value of 7 mm. Hence for such precision it is better to use a vacuum-walled vessel or the adiabatic method. The convection shield is not always satisfactory for this high precision. For 0.3 per mille precision, the highest yet actually reported, it is adequate, and it has the advantage of simplicity.

5. Error from this source can be detected by comparing similar temperature rise curves, or by studying the segments along them (*ab-bc*, etc., of Fig. 6). The remedy for any error is to improve the frequency or timing of the observations, to use the combination method of page 57, or to protract the temperature rise. This last can always be done if necessary. A lessening of the thermal leakiness, K, also lessens the effect of the error in determining φ_x.

Chapter III

Methods In General

Of importance in calorimetry are a number of experimental rules or principles which are far from new, and whose applicability is by no means confined to that branch of research. Yet these appear to be forgotten often enough, or are sufficiently undefined, so that a mention of them here seems in order.

Section 13. Systematic Discussion of Experimental Efficiency

The whole plan of the present book illustrates one method in scientific work, namely, the guidance of experimentation by analysis of the various physical processes and sources of error concerned. This is more or less an extension, first, of what everyone does who sets out to make a plan for experimental work, and second, of the investigations, published all too rarely, of the performance of particular installations or methods.[1] Its main idea is not instruction, tho it should have some value as such, but the development of the subject thru criticism and discussion, which itself should be the object of further criticism and discussion.

In the present case there has been no hesitation in dealing with elementary matters which do not so often get discussed. Mistakes and oversights regarding such are by no means impossible, and when they do occur, are much more likely to escape scrutiny. For instance, more than one really eminent experimenter has been known to suggest that a large leakage modulus is not detrimental in the adiabatic method, because the adiabatic adjustment prevents all thermal leakage anyway—a proposition whose falsity scarcely needs the demonstration of it which is repeated in this book (*see* footnote, page 50).

Section 14. Experiment, Reasoning, and Reason

Deductive reasoning plays a large part in this discussion of calorimetry. This brings up the general question of deduction vs. experi-

[1] The investigations of the adiabatic method, published about 1906 by Richards and colleagues, and above all, Barry's unrivaled development of that method, are a very gratifying illustration of this kind of work. On the other hand, there is every indication that calorimetry at low temperatures by the electrically-heated aneroid suffered severely for a dozen years from a lack of discussion and of understanding of the principal sources of error.

ment. Ideally, experiment and deduction should both be consulted; an uncriticized experimental result will be an uncertain guide where different conditions are to be met, and may be misleading if a change occurs in some factor whose importance is not realized. For if almost any deductive or "logical" system is examined, whether in physics, political economy, or the building of one-horse chaises, it will nearly always be found that, in spite of all that is said in disparagement of "logic," the logic itself is not at fault; the trouble is that something has been overlooked in the premises. But if something is likely to be overlooked in applying a carefully derived logical result to some concrete case, something is much more likely to be overlooked in applying a purely experimental result to a different set of circumstances. A specially important instance of this is the fact, easily seen and often neglected, that the precision obtained by a method or an installation under some circumstances may not appear under others.

A Possible Misapprehension

One thing may be misunderstood in the present discussion. The conditions specified for precision here are such as to give a close approach to certainty; that is, even slightly excessive error only once in several hundred experiments. But the average worker may, or must, judge his precision by the agreement of less than a hundred. He might suppose that the requirements laid down here are unreasonably severe. There is no real conflict, however, with his practical result. There are merely two different degrees or standards of precision in question.

Where Deduction Excels Experiment

One advantage possessed by the deductive treatment of errors is the ability to deal when necessary with errors that cannot be reached at all by experiment alone. A purely experimental final result can hardly give reliable information about errors that are not larger than its own accidental error. But if several small errors are present nearly every one of them will usually be considerably smaller than the resultant accidental error. On the other hand, the preceding part of this book illustrates how such errors can be treated by deductive methods.

Examples of Successful Deduction or Analysis

This book presents cases where pure deduction, the analysis of a calorimetric process, has played the part of inventiveness in producing new methods. Four instances of this are:

The Second Geophysical Laboratory Method. A recognition of the true origin of some ordinary calorimetric errors pointed to this

method as giving the brevity of some other methods without their loss of precision.

The General Law of Lags. In a matter scarcely accessible to experiment it has been shown how the serious errors once threatened by lags can be avoided; namely, by simply letting the lags alone—which involves having them and the jacket temperature constant.

Development of the Adiabatic Method. The more convinced experimenters were that with the adiabatic method (Section 16) they had got a lessening of thermal leakage error the less they got it, for the very conviction that they had it already led them to neglect securing the thick air gaps which would really have given it. The study of convection showed that the adiabatic method, by practically eliminating convection, enables thick air gaps to be employed safely, with a consequent lessening of thermal leakage error. The method which does lessen this error is thus in part a product of deduction.

Improvement of the Convection Shield. The metal shield in the air gap, long known, has been made practically a new device now that study has shown (1) the true source of its value, namely, the lessening of convection, and (2) the vital importance of having it very thin.

Section 15. Hunting for Sources of Error

When an experimenter finds that the precision of his work is less than he had calculated or judged that it would be, he may, according to circumstances, make more or less of an attempt to find the cause. There are two reasons for spending time in this way. First, apparently accidental discrepancies, which will usually be the things observed, are liable to be the variable part of some larger effect, which is apt to cause also a systematic error. Second, even if the error is largely accidental it is, if unexpected, presumably due to some unknown cause, and this cause is likely to be removable. Hence it may be easy to increase the precision considerably if the trouble can be located.

The finding of such sources of error is often very interesting. The experimenter has, at first, merely a record of variations in final results. In order to discover the hidden cause he must find or make his own clues, and then apply them by a process of inference that is apt to suggest the labors of Sherlock Holmes. It is rather inefficient, however, to provide such amusement for the experimenter where it can be avoided; moreover, if the task is too difficult even the amusement disappears and the source of trouble may not be found at all. The difficulty evidently increases very rapidly as the number of possible sources of error to be examined becomes greater. Hence those who

expect to eliminate avoidable errors will do well to suppress as many sources of error as possible at the start. This does not mean to make the errors improbable; it means to make them practically impossible. In a carefully planned system all excessive errors are improbable, yet it is among such that the actual error must be found.

For instance, an insidious error occurring in a calorimeter where the adequacy of the stirring was a little doubtful caused a good deal of time to be lost in an investigation of the stirring, which happened to be unusually difficult to make. The stirring was adequate; no mistake had been made in the design. But if that had been *certain,* time would have been saved.

Examples of Improbable Errors

Some errors are very unexpected; hardly to be identified at all unless the number of other possible errors is small. For instance: (1) Slight quantities of water evaporating from a calorimeter and accumulating in the chamber finally produced condensation effects that spoiled an important investigation. The evaporation had been carefully measured; the accumulation was long unsuspected, and would have been considered improbable by almost anyone until it was proved. (2) I have elsewhere recorded a case of error thru steam production in dropping hot bodies into water,[2] which is hard to account for even now, and was established only by a comparison of results extending over more than a year. (3) Another instance which occurred in my work was where in a joint near the top of the calorimeter a fine crack opened, which leaked only when the calorimeter had been heated. The discovery of this came thru a test for evaporation, made by weighing calorimeter, stirrer, and thermometer after the experiment without losing any water.

Making Errors "Impossible"

What is necessary to make an error practically impossible will depend on the source of the error and the precision desired, and is one of the questions which this book is intended to help in answering. Thus, to make the jacket temperature error quite negligible might call only for a completely inclosing jacket in work of moderate (1 per mille) precision, while for high precision, where the jacket would be complete in any case, it might call, in addition, for specially large stirrers and passages, and other means of promoting temperature uniformity.

[2] White, Walter P., *Am. J. Sci.,* **47**, 54-7 (1919).

Aids in Detecting Errors

One of the most effective instruments for detecting errors is a thermometer so sensitive that its own errors do not interfere. This may be called putting the thermometric error in the impossible class. Sometimes errors can be tested specially; which is quite sufficient when the test shows, as it usually will do, that the error is negligible. For instance, irregularity in the rate of stirring can be checked by a revolution counter; differential temperature measurements with thermels may reveal various irregularities and failures of temperature uniformity. These detectors can, if necessary, often be used during regular work, and this may be highly important in difficult cases. If an occasional or very irregular effect is sought the attempt to watch for it and do nothing else is very slow and uncertain.

Just how far to go in eliminating sources of error is a question for judgment rather than formula. It is a question of the relative cost of making the error impossible, and of experimenting to find whether it is occurring, if it is possible.

Dispensing with Tests of Efficiency

A similar problem may arise regarding tests made during the try-out of an installation to see how accurate or reliable certain features of the apparatus are. A little consideration may often show that the test costs more than making the apparatus so sure that that test is not needed. Illustrations of this are the providing of very large jacket stirrers; the using of metallic covers instead of poorly-conducting ones of larger lag and less uniform temperature; the use of governors for stirring motors; the blanketing of exposed surfaces; for 1 per mille precision the provision of covers and other precautions which are strictly necessary only in more accurate work.

Such contrivances often are not very expensive. Frequently, indeed, if they are rejected it is not on account of expense, but because they seem a complication, or of no great value.

In considering such rejections designers of calorimeters must often have recognized in themselves or others a tendency to permit the ease of construction of the apparatus, which is immediately ahead, to take on too much importance compared to the manipulation that comes later. Much the same is true of the praise often given to "simplicity." What is meant is usually merely simplicity of construction; but simplicity of construction often means complexity of operation and vice versa.

Chapter IV

Particular Methods

Section 16. The Adiabatic Method

Its General Value

The adiabatic method, first used by Person (1849), and brought to the fore by T. W. Richards, has probably aroused as much interest and been as much misunderstood as any in calorimetry.

Curiously enough, the very errors which it has often been supposed especially to diminish, namely, those from lag and from the thermal leakage proper, are precisely the ones which it has usually tended to aggravate.

Error in the Thermal Head, q. In the case of the thermal leakage this has come thru confusing the amount of such leakage with the amount of error involved in it. The error is in the measurement or adjustment of a temperature, and has almost nothing to do with the difference between this temperature and some other; that is, with the size of the thermal head. It has been pointed out, in this book and elsewhere,[1] that the adjustment nearly always has involved more error than the following of the smooth calorimeter temperature curve. The adiabatic method has succeeded in spite of this error. The importance of restricting it has been realized by practical workers with the method, who have sometimes reported a maximum error of 0.02° in the adjustment of φ_x. If the effective duration of this maladjustment is 2 minutes the resulting final error, φKT, will seldom exceed $0.02° \times 0.003 \times 2$, or 0.000 12°. The error due to φ_x is thus very small in Richards' adiabatic method. But the corresponding error in the ordinary method is still smaller, and this fact has often been misapprehended.

It seems desirable that those reporting on this error in φ_x should give it in terms of time also, since when stated in this way it is more nearly the same for different rates or temperature intervals, and on multiplication by K gives at once the proportional final error due to

[1] *See e.g.* Dickinson, H. C., *U. S. Bur. Standards Bull.*, **11**, 206-7; White, Walter P., *J. Am. Chem. Soc.*, **40**, 389 (1918).

itself. When expressed as a time it has some of the characteristics of a lag, and may be called "experimenter's lag." It has already been discussed in the section on timing.

The expression, thermal leakage "proper," as used here does not include leakage from evaporation. The methods of dealing with evaporation are so different from those concerned with conduction, that I have thought clearness would be promoted by putting it in a separate class.

Lag in the Adiabatic Method. Altho there is no good reason for thinking that the adiabatic method diminishes the thermal leakage error proper, the notion that it eliminates lag error was quite reasonable at one time. Two lags then were chiefly in mind; the lag of the thermometer, and a possible lag of the air currents around the calorimeter. Subsequent work has shown that this latter lag is inconsiderable, and that the lag of the thermometer can be and usually is eliminated completely without the adiabatic method. The real effect of the adiabatic method on lag error is as follows: (*a*) Lags in and of the calorimeter, since they depend on its temperature change alone, are not affected. (*b*) Lags of shields are modified, but not so as to result in any great advantage or disadvantage. (*c*) Lags in the jacket are added. (*d*) Instead of the two thermometer lag effects of non-adiabatic working, which cancel each other with almost mathematical rigor when the same thermometer is used thruout, there are substituted simultaneous lags of two different thermometers, which neutralize only when the thermometers are alike, similarly placed with respect to the heat-conveying surfaces, and exposed to equally vigorous stirring. If these requirements are not perfectly met, the resulting lag, if constant, will still cause no error after a direct calibration. But this is true of all constant lags. And if the jacket stirring varies, the thermometer lag and other jacket lags will usually vary and become a source of error.

These lags are small, but they are still comparable with thermometer lag. Unusually well stirred jackets and calorimeters have been observed to have stirring lags of 10 seconds. If only half of this is effective between thermometer and heat-emitting surfaces, the resulting lag, 5 seconds, is about as large as the smallest, 6 seconds, usually reported for calorimetric mercury thermometers.

(*e*) Compared with the cruder methods mentioned on pages 87 and 124 in which no thermometric observations are made during the temperature rise, the adiabatic may diminish lag error because it eliminates completely the thermometer lag of the final temperature. This point, however, is of little more than historic interest, since with experimental

calibration the error from these lags is eliminated. Indeed, with experimental calibration the only lag errors surviving are those due to variation in the amount of lag. These occur ordinarily only in the stirring lags, regarding which the adiabatic method, as already shown, is somewhat at a disadvantage.

(f) All lags, whether constant or not, may cause error if the jacket temperature varies, the error being εLK, if ε is the percentage variation. The adiabatic method avoids this source of error because in it the jacket temperature must necessarily be attended to.

(g) When the adiabatic method is used to secure a thicker air gap, and therefore a smaller thermal leakiness, K (page 119), the error from all lags, including stirring lag, is lessened, in accordance with equation **L2** (page 87), where $LK\Delta\Theta$ is that error. In this indirect way the adiabatic gives about the same benefit as the convection shield or the vacuum-wall.

Elimination of Leakage Modulus Error. Turning from the deficiencies to the advantages of the adiabatic method, the elimination of error from variation in the leakage modulus, K, which follows directly from the very small value of its multiplier, the thermal head, φ, is of the most importance to the progress of science. It is practically indispensable in protracted experiments, for which the term containing K as a factor would, without the adiabatic method, sometimes be about as large as the main temperature rise. The chief source of the eliminated error is the variation in K due to convection. The adiabatic method really destroys this source of error in two ways, either of which alone would be sufficient; it reduces the convection as well as its multiplier nearly to nothing.

In the much more numerous brief experiments the adiabatic method is less important. In these convection can, as has been shown, be handled in several ways, hence the relative value of the adiabatic method depends on the balancing of various lesser advantages, and may be more or less a matter of individual preference.

The advantage most welcome to many experimenters has been the elimination of the large and uncertain error which comes thru distillation of the calorimeter water. Very often the statement that the adiabatic method lessens thermal leakage—or "cooling correction"—error refers mainly to this feature, classing evaporation as a part of the thermal leakage. The advantage, however, exists only with uncovered calorimeters. With respect to it the adiabatic might almost be called a license to use an open calorimeter. And as such it may come near being a detriment in disguise, for the adiabatic alone gives a less

complete elimination of evaporation errors than could be obtained in other ways if the experimenter did not feel that he was free from the need for them. This will be shown presently.

The adiabatic method with the open calorimeter has nevertheless given what is generally regarded as a high degree of precision. But it can hardly give as much as modern methods, adiabatic or otherwise, can give when evaporation is efficiently controlled. Hence it seemingly makes for clearness in discussing evaporation to speak of the adiabatic method as a substitute or rival of a tight calorimeter cover.

Large Intervals Facilitated. The double elimination of convection effects which the adiabatic method affords allows large temperature rises to be used successfully, so diminishing the important temperature measurement errors.[1] This point seems to have attracted little attention.

Smaller Leakage Modulus Secured. For the same reason relatively large air gaps can safely be employed and a small leakage modulus thus secured.[2] The small modulus, in turn, is especially advantageous to the adiabatic method as an offset to the large thermal head error which accompanies its small thermal head. But the permanent installation of a wide gap confines the experimenter to adiabatic work only. A convection shield gives the same advantage without the disadvantage.

On the other hand, since the adiabatic method eliminates convection so thoroly, it can at the same time secure both large temperature rise and small thermal leakiness, thus lessening the two most serious errors, those from the thermometer and from the stirring lag. The convection shield will accomplish either, but not both at once to the fullest extent, and neither very well in some cases where extreme precision is sought. (See Table VII.) The use of a vacuum wall (Thermos bottle) diminishes at the same time both convection and thermal leakiness.

The very thin gaps, sometimes as little as 2 mm., whose smallness necessarily brings a very large thermal leakiness, K, that have been used with the adiabatic method, were adopted not inadvertently, but to lessen the heat capacity of the air, or the saturation effect from evaporation. The first reason ceases to be valid where experimental calibration is employed, as it should be in the best work; if any such lessening of the gap is best on account of air saturation it follows that the advantage of the adiabatic in lessening the error due to evaporation from open calorimeters is bought at the cost of a perhaps

[1] White, Walter P., *J. Am. Chem. Soc.*, **40**, 388-89 (1918).
[2] *Ibid.*; Barry, F., *ibid.*, **44**, 931 (1922).

tenfold increase in all the errors which increase with K, if comparison is made with methods, adiabatic or other, where evaporation is restricted. These errors increasing with K include the stirring-lag error, all other lag errors, timing errors, errors from imperfect observation or adjustment of the temperature rise and thermal head. The open calorimeter, therefore, despite the high precision it has yielded, has almost certainly fallen short of the maximum precision attainable with the adiabatic method.

Effect on Evaporation Error. It has just been pointed out that the lessening of evaporation error which the adiabatic method gives exists only for uncovered calorimeters, and is less complete than that obtained thru a tight calorimeter cover. Since a tight cover is easier to provide and maintain than the adiabatic method is, and since the nearly tight cover, often very desirable, works well without the adiabatic method and not so well with it, evaporation alone will seldom provide a good reason for the use of that method. In doubtful cases the question of evaporation might perhaps turn the scale, and when the adiabatic method has once been selected it will often enable the experimenter to get along without covering his calorimeter. But the adiabatic method reaches its highest precision only when freed from the burden of preventing distillation. One reason for this is found in the phenomena of adsorption, as pointed out in the section on evaporation; another, mentioned a few pages back, is the thinning of the air gap which is needed, or at any rate desirable, where saturation error threatens. The chief advantage of the adiabatic in shorter experiments, namely, the lessening of the thermal leakage error proper, including lag-, time- and stirring-errors, which comes with a thick air gap, is incompatible with evaporation.

In a vacuum-walled calorimeter the disadvantages of evaporation with the adiabatic method largely disappear, while a tight cover, in addition to the jacket cover, is relatively inconvenient. Hence if such a calorimeter is to be used anyway there is very strong reason for handling the evaporation by means of the adiabatic method. But if the adiabatic method is to be used at all it can make the vacuum wall unnecessary, as Barry has shown.[3] This, however, involves preventing all evaporation.

Saving of Computation. Very strong emphasis has been laid[4] on the advantage of avoiding the computation of the "cooling correction." But since a Regnault-Pfaundler correction usually can easily be calcu-

[3] *J. Am. Chem. Soc.*, 44, 931 (1922).
[4] Daniels, F., *J. Am. Chem. Soc.*, 38, 1474 (1916).

lated in 3 minutes, with part of this work done during the observations, and since the adiabatic method requires some extra manipulation, the gain in time by its use is nearly nothing. The avoidance of possible arithmetical mistakes in the calculation may be of importance—how much, of course, depends on the personal equation.

Facility in Following Abrupt Temperature Rises. As is hinted at in the section on timing, page 61, the adiabatic method may render it easier to follow abrupt changes of calorimeter temperature, being somewhat comparable in this respect with the new special method of page 57.

The Real Accomplishment at Harvard. In 1909, in an address on progress in Thermochemistry, Professor T. W. Richards suggested that all other errors in calorimetry, including those of mercury thermometers, were trifling compared to those from thermal leakage, but that these were greatly diminished by introducing the adiabatic method. This former opinion of a leading worker in calorimetry is strikingly at variance with the conclusions presented here. These are that thermal leakage proper can usually be made to cause less error than ordinarily comes even from electric thermometers, and that the adiabatic method, in spite of the considerable special advantages just listed here, does not, in ordinary short experiments, and in calorimeters with narrow air gaps, diminish materially the main thermal leakage errors. The difference, however, is easily accounted for. Richards had only uncovered calorimeters in mind, and his "cooling effect of the surroundings" (thermal leakage) included evaporation, and so defined certainly had less error with the adiabatic method. The non-adiabatic calorimeters of which he spoke were crude affairs prevailing at the time, having much larger errors in the thermal leakage proper than are here considered normal in precision work. So far, then, Richards' statements, properly understood, are quite consistent with those in this book. The discrepancy arises thru his not including as a part of the adiabatic method certain technical improvements, especially complete jacketing, which, tho adopted by him in developing that method, were independently introduced by others. These improvements, with a few more, are here taken to be the regular order in precision calorimetry. Modern precision calorimetry, then, is simply the sort of thing which Richards took the lead in introducing, and which he offered as a remedy for thermal leakage errors. There is clearly no disagreement with him in saying that it is such a remedy. But it is not the adiabatic method, and the chief thing which Richards did get from that method, namely, lessening of evaporation error, can be perhaps better obtained by other

means. In long experiments, where convection error is formidable, and in some aneroid work, the adiabatic method is desirable or indispensable, and so are Joule's twin calorimeters for special thermometric precision, but in general it is effective control of measurements and conditions, rather than any special "method," that is the main factor in precision.

Practical Details of Adiabatic Working

Methods of Heating. Richards originally suggested three methods of heating the jacket. The one he selected, neutralization of alkali by acid, is evidently able to give an easy and precise predetermination of the temperature change to be produced, and almost any desired degree of speed in making even large changes. By using an ingenious pipet of varying cross-section and slope [5] Richards and Davis have even had the whole neutralization accomplished automatically at a varying rate determined before the experiment began.[6] Most other experimenters, however, have used one of the other two methods. Hot water can be run in as easily as acid, and has been considerably used. The change of temperature produced by it varies with the jacket temperature, but this complication does not seem serious. Barry used it as an emergency measure, in addition to acid and alkali. Weiss, Piccard, and Carrard [7] used an ingenious control scheme with hot water heating, which could be used still more easily with acid. The calorimeter temperature was followed with an electric thermometer having a slide wire drum. A cord unwinding from a part of this drum lowered a plunger, which displaced the hot water from a reservoir, to flow into the jacket. Hence the amount of water already delivered at any time, and therefore the jacket temperature, was governed by the calorimeter temperature change up to that time.

A plunger moved along a scale graduated in degrees of jacket temperature, and used to match the calorimeter temperature as read, is a simpler device suggested by the above. It would in operation and precision closely resemble Richards' scheme of running liquid thru a stopcock from a burette graduated in jacket degrees, but seems on the whole easier of manipulation.

Electric heating of the jacket, the third method, has been much used. It has some evident advantages in convenience, tho it is not very easily

[5] Richards, T. W., and Davis, H. S., *J. Am. Chem. Soc.*, 39, 347 (1917).

[6] In itself, this method evidently amounts to taking the temperature rise curve as known in advance, as in J. D. Davis and Wallace's short method (page 125). But the experimenter, relieved of manipulation by the automatic device, might take very accurate readings of the thermal head, and then apply a correction for their difference from zero.

[7] Weiss, P., Piccard, A., and Carrard, A., "Calorimétrie des Substances Ferro-Magnétiques," *Geneva Archives*, 43, 30 (1917).

adapted to following very rapid changes in the calorimeter. It is especially suited, however, to 2 superior methods of making the adiabatic adjustment. One, suggested by Dickinson, is to run a smooth curve with the jacket, and compute for the small thermal head resulting. This eliminates by computation the error of adjustment. The other, used by Barry [8] (who actually used acid and alkali, however), is to make the thermal head oscillate regularly between small positive and negative values. The mean is then nearer zero than when an effort is made to follow the calorimeter curve exactly.

Electric Heaters. The lag of some electric heaters is too great for satisfactory adiabatic work, but heaters with a lag as low as 3 seconds can easily be made, and since they can be distributed thru the jacket, if this is desired, their neutralization of the stirring lag should largely make up for their own lag. Swientoslawski and Pakovich [9] used kerosene as a jacket fluid in order to be able to immerse bare heating wires in it, but MacInnes and Braham [10] apparently did better by putting the bare wires in water, using alternating current. Kerosene, on account of its low specific heat and small thermal conductivity, is far inferior to water in carrying heat, as Harper has shown experimentally.[11] Swientoslawski subsequently described a water-filled jacket, regulated by hot and cold water. A smaller lag and more complete distribution even than MacInnes and Braham's was reached by Daniels,[12] who passed alternating current directly thru the jacket water. He reports a maximum lag in the adjustment of 2 seconds, which is less than the lag of the galvanometer which guided the regulation. Daniels [13] has described an automatic regulator depending on a selenium cell, and Richards, one operated by a differential air thermometer.[14] The photoelectric cell with triode tube seems now to have recommended itself as the best instrument for such tasks. But there are reasons for thinking that the observer is the best regulating device, after all, in adiabatic work [15] for experiments of moderate length.

MacInnes and Braham's Modification. MacInnes and Braham maintained a thermal head of about 0.15° in order to counteract the heat of stirring and keep the calorimeter at a constant temperature thruout. Their chief reason was to facilitate the temperature measure-

[8] Barry, F., *J. Am. Chem. Soc.*, **42**, 1922 (1920).
[9] Swientoslawski, V., and Pakovich, I., *J. Russ. Phys. Chem. Soc.*, **46**, 1284 (1914).
[10] MacInnes, D. A., and Braham, J. M., *J. Am. Chem. Soc.*, **39**, 2110 (1917).
[11] Harper attributed the difference he found to difference in viscosity. But the arrangement he used was specially and admirably designed to eliminate the effect of viscosity.
[12] *J. Am. Chem. Soc.*, **38**, 1475 (1916); Derby, J. H., and Marden, J. W., *J. Am. Chem. Soc.*, **35**, 1767 (1913).
[13] *Op. cit.*, p. 1477.
[14] Richards, T. W., and Osgood, C. D., *J. Am. Chem. Soc.*, **37**, 1718 (1915).
[15] Daniels, *op. cit.*, p. 1479.

ments with the resistance thermometer. But (1) The resistance thermometer technic which demands practically stationary temperatures to measure is unnecessary and objectionable;[16] (2) If the heat of stirring had been as small as is recommended in this book (Section 7) the authors could have read well enough even with their installation; (3) Their modification demanded considerable time for finding the proper thermal heads; (4) In their particular case the initial thermal head necessitated making a different mixing chamber for their thermochemical work. Hence, while their method should be kept on the list, it does not seem to merit a general recommendation. It is now known that their thermal leakiness was at best 4 times as great as it had any need to be. Otherwise their counteracting thermal head would have been 0.6°.

The Constant Rate, w, in the Adiabatic Method. It has already been said that the adiabatic adjustment does not eliminate the constant rate, w. In general a rating period is run to determine w. In the cases where the adiabatic method is especially useful, namely, the long-continued experiments, the determination of w, if needed at all, will need as much more time as the X-period itself. Thus maximum precision in determining a 4-hour reaction might call for 8 hours. It will evidently be highly desirable to have w so constant that frequent determinations of it will not be needed. The stirring can doubtless be kept as constant from day to day as it can be kept for 4 hours. It will then only be necessary to avoid flow of heat thru the jacket, and error in the measurement of φ. The first can be secured by putting the whole installation in a constant-temperature closet, a precaution already taken by Barry.

Section 17. Short Methods

Computational Only

Many short methods are merely approximations in the temperature loss computation. These seem in the literature to have been taken fully as seriously as they deserve. One of the simplest and most frequent is taking the temperature loss as equal to the loss in the single rating period. This amounts to treating the temperature rise as instantaneous; it ignores the area $A\tau$ of Figure 5. The resulting error may be of the order of $KA\tau$, approximately $K\tau\Delta\Theta$, or frequently $0.002\Delta\Theta$, but (footnote, page 42) it is likely to be much smaller than this, and may be almost nothing. Hence it is well, in planning or using this method, to investigate the relative magnitude of q_x and φ_r, the mean thermal

[16] White, Walter P., *J. Am. Chem. Soc.*, **48**, 1148, footnote (1926).

heads for the two periods. It may thus be found that the results are highly accurate, while otherwise there will usually be no assurance of this. Even if the difference $\varphi_r - \varphi_x$ is not so very small, there will be practically no error if $\frac{\varphi_r - \varphi_x}{\varphi_r}$ is approximately the same for different experiments, and if the calibration is experimental with the same value of $\frac{\varphi_r - \varphi_x}{\varphi_r}$ also.

The only time these methods save is that needed for a more accurate calculation, and this is less than a minute more than what can be done during the rating period. Its amount is sometimes greatly exaggerated.

By Omitting All Rating Periods

Since one of the two Geophysical Laboratory methods will nearly always be advantageous, and each of them needs only one rating period, the only way to really save time is to eliminate all rating periods. This, for the same precision, requires a far better knowledge of w, and perhaps K, and therefore far greater day-to-day constancy in them. The single period in either Geophysical Laboratory method gives the immediate effective value of both w and K, save for a small term calling for an imperfectly known value of one or the other. Hence the speed of the rapid method is bought either by a loss of precision or by the labor of providing the unusual constancy. A case where both speed and constancy are well worth having has already been considered under the adiabatic method, namely, protracted accurate determinations, where the "speed" may mean saving 3 to 10 hours.

Methods with Small Value of φ_x. If the thermal head φ_x in the experimental period is made to be near zero all need of great constancy in K disappears. This may be secured by the adiabatic method, or by a method, otherwise like Rumford's (Section 3 § 5), in which φ_x is measured, after the initial conditions have been so chosen as to make it near zero.

For such cases the value of w, the constant rate including the heat of stirring, must be known so well that wT_x has no perceptible error. Where observations are needed to give the value of w, methods with resultant φ_x near zero are detrimental.

Omitting the φ_x Observations

Davis and Wallace,[17] who omitted the rating period, omitted the φ_x observations also, thereby saving a little time in the middle of the

[17] Davis J. D., and Wallace, E. L., *Bureau of Mines, Tech. Paper* 91 (1918).

X-period. They also saved some computation, for the integrated φ_x was taken as a function of the temperature rise, and so, also, was the temperature loss, K being constant. Apparently the experiments might have been so run as to make φ_x near zero, but probably without any advantage. At any rate, an agreement of 1 per mille was pretty consistently attained, demanding both a constant K and w and a constant form of the temperature rise curve. The jacket was thermostated.

Section 18. Joule's Double, or Twin, Calorimeters

In first proposing the twin calorimeters Joule was primarily trying to adapt electric heating to calorimetry, but was restricted by the difficulty which then existed of determining easily and accurately any electric quantity except resistance. The twin scheme got around this difficulty. Then a necessity, it is still an advantage in simplifying the electric manipulation.

Pfaundler's addition of the differential thermel was in line with Joule's work, and is very important. But the twin idea, and even the adjustable mercury heating resistance described by Pfaundler, were dsecribed by Joule 24 years earlier, tho Pfaundler does not mention this.

Advantages and Disadvantages

The twin calorimeters evidently are not adapted to all kinds of work. Where they are available, they have the following advantages:

Temperature Measurement. Foremost of all, temperature measurement from four to ten times as accurate, absolutely, as by the best methods of reading temperature change directly, and yet obtained with far greater ease. This is due: (1) to the fact that the potentiometer measures a bare correction term, far less than the quantity measured by the potentiometer or bridge with a thermoelectric or resistance thermometer as ordinarily used; (2) because the thermel becomes practically errorless when there are no considerable gradients along it. In order to secure this advantage the middle portion of the thermel must be so treated as to be at the same temperature as the ends in the calorimeters. This is easily secured if the jacket at each final reading is at the same temperature as the calorimeters, while no part of the thermel is exposed to the outer air.

The Heating. The equal heaters, taking the same current, are a very simple and accurate means of providing equal heat. They are, however, in no wise a means of measuring heat quantity. In order to measure heat electrically the electric energy must be measured. The

Joule calorimeters with duplicate heating really measure the heat capacity of one body in terms of that of another.

Heat quantities can be compared with these calorimeters; heats of reaction, for instance. But with such, the measurement of that which produces the heat is not in the least affected by having the two reactions carried out simultaneously in two different vessels. The heats can be produced quite as accurately successively in the same one. Indeed, this is often the most accurate way to proceed even with the twins, measuring both quantities in the same calorimeter, and having in the other a third reaction which, repeated, serves as a medium of comparison between the other two, and is used only to gain the advantages of the duplicate method, chiefly with respect to temperature measurement.

Compensation of Thermal Leakage Effects. It is evident enough that the differential temperature, the thing measured, changes very little if both calorimeters are heated alike, and much importance has sometimes been attached to this fact. But there are hundreds of cases in Physics where reducing some effect *almost* to zero does not correspondingly reduce its *error,* and this is one of them, as will appear in the next paragraph.

Treatment of the Thermal Leakage

Repeating some equations which I gave some time ago:[18] Let $\Theta_a\Theta_b$ be the temperatures of two twin calorimeters

K_aK_b their thermal leakage moduli.

C the jacket temperature.

Then for each, $d\Theta/dt = (C - \Theta)K$ and:

$\frac{d}{dt}(\Theta_a - \Theta_b) = K_a(C - \Theta_a) - K_b(C - \Theta_b)$, which transforms to

$$d/dt\ (\Theta_a - \Theta_b) = K_A(\Theta_b - \Theta_a) + (K_a - K_b)\ (C - \Theta_b) \quad \textbf{(34)}$$

Since the heat going from one calorimeter directly to the other depends upon $\Theta_a - \Theta_b$ only, its coefficient is included in K_A.

We thus have two effective leakage moduli, one normally large, the other, $K_a - K_b$, very small, and two thermal heads, one very small and the other large. Both the terms concerned, the first and second of the second member of Equation **34,** can be handled by means of two rating periods with different values of $\Theta_a - \Theta_b$, but few will care to do that, except in the preliminary studies of the apparatus. In cruder work $K_a - K_b$ can be made very small, and then neglected. In more refined work the adiabatic method is added[19] and the second term

[18] White, Walter P., *J. Am. Chem. Soc.,* **36,** 2315 (1914); *ibid.* **40,** 1895 (1918).

[19] Davis, J. D., *Ind. Eng. Chem.,* **16,** 726 (1924); Richards, T. W., and Gucker, F. T., *J. Am. Chem. Soc.,* **47,** 1876 (1925).

becomes quite negligible. Richards and Gucker actually kept $\Theta_a - \Theta_b$ so small that the first term also was negligible. They ran a rating period, which cared for difference in stirring heat and evaporation, and possibly other slight effects.

Secondary Advantages of Twin Calorimeters

Applying to the twin calorimeters the list of important sources of error given in Section 12:

The temperature measurement error is notably decreased.

The error from heat of stirring can be diminished by giving the two stirrers the same speed. I have read of a very neat scheme for doing this. The two stirrer pulleys are joined by both a belt and a connecting rod. The noise of gears, besides being disagreeable, shuts off the valuable information which other sounds often give as to the functioning of the apparatus.

Evaporation error tends to be eliminated thru similarity of conditions. Care can greatly increase this advantage.

Convection error is eliminated for the same reason, and so is the usually negligible error in following the temperature rise.

The twin calorimeter method and the adiabatic method together confer a freedom from thermal leakage error which neither alone affords as well.

If liquids of different viscosity or vapor pressure are being compared, the elimination of evaporation or stirring heat error may not be altogether complete.

Exchanges and Other Checks on Errors

Many experimenters with Joule's calorimeters have sought to eliminate the effect of dissimilarities by exchanging the charges of the calorimeters, and an exchange of heaters has also been mentioned. (In work of very high precision it will be well to take care that the arrangement of the heater leads is constant, both as to depth of immersion and excellence of contact with solid bodies. *See* Section 20.) If the dissimilarities are small and constant, the exchange gives a practically perfect elimination of their effect, yet with no greater number of observations than are needed to deal with accidental errors. At the same time the average of the differences shown on exchanging gives the value of the true difference as well as any other method can. To exchange the heaters separately does not seem to add anything to the accuracy obtainable by the same number of observations without this particular exchange.

Special Observations. If a more thoro knowledge of the calorimetric system is desired, exchange of heaters may help, but certain other observations seem equally important. These are:

(1) Rating periods, showing the difference in spontaneous change of the calorimeters, and especially showing differences in evaporation when other causes of difference are separately determined;

(2) Variation of the speed of stirring, to eliminate or exaggerate differences in the stirring heat produced in the two calorimeters;

(3) Rating periods with one or other of the two thermal heads rather large, to exaggerate and so measure the effect of not keeping each of them near zero.

Such tests may be necessary if liquids of different viscosity or vapor tension are compared, since there then might be differences in evaporation, stirring heat, or thermal leakiness (K) which evidently would not be eliminated by reversals.

If reversals are undesirable (as with Richards and Gucker, where one calorimeter was of platinum, to handle corrosive liquids) the difference between the calorimeters can be determined by running both with the same fluid. Differences due to the liquids can then be dealt with by rating periods, etc., as in other cases. This scheme does not take care of differences in calorimeter behavior which vary with the liquid. These are a matter for special study where reversals are impossible. Usually help can be obtained by using liquids of different properties, even if the exact properties of some, *e.g.* corrosive, liquids cannot be obtained in both calorimeters.

Differences in calorimeter behavior varying with the liquid may arise if the liquids have different heat capacity, conductivity, or viscosity, and the calorimeter walls also differ in emissivity, or in conductivity, owing to difference in material or thickness, or there are differences in the stirring or the heaters. The combined effect of such differences cannot be found exactly by determining them separately, and the important effect is that during the heating, which cannot be investigated in rating periods. Of course such effects are likely to be important only in very accurate work.

Differences in Amount of Liquid. Where liquids of different volume specific heat are compared (*e.g.* kerosene, about 0.4, water about 1.0) if the calorimeters are filled equally full the heat must be made unequal in some way, and the thermal leakiness will be unequal. It seems better to take about equal heat capacities, and then put in one calorimeter some kind of an inclosed air space so that the depth of liquid, and therefore the effective heat capacity of the calorimeters

themselves, may be kept nearly equal. The resulting differences in heat and effectiveness of stirring, and the minor differences in thermal leakiness, can be investigated by rating periods, etc., as in other cases. The need here is somewhat greater than usual.

The usually small errors detected by rating periods, etc., are important, first because these errors are otherwise thoroly concealed and systematically variable with the different substances compared; second because the thermometric and some other errors of the twin method are so exceptionally small that correspondingly small values of other errors are often desirable.

The Twin Method for Solids

Altho the twin method has usually been reserved for liquids its employment for determining the specific heats of solids is no new suggestion. If the solid is immersed in the vessel of liquid and heated with it there is an evident loss of sensitiveness, since a given error in temperature measurement, and therefore in the heat capacity as determined, will appear as an error in the heat capacity of the solid, and will seem greater as the relative amount of solid is less. But if the specific heat for a small interval near the calorimeter temperature is found from the difference of two determinations by the method of mixtures for the same solid, the effect of the calorimeter temperature error will, as can easily be shown, be about the same. Since the solid can usually be larger in the twin method, and the calorimetric precision greater, the final error will actually be less, while the errors due to the heater of the solid and to the transferring from it will disappear. The real rival of the twin method for such work is the electrically-heated synthermal aneroid. The amount of dead material is less in the aneroid, tho this is apt to be offset by a smaller thermometric sensitiveness, even with the twin aneroid used by Gaede, the originator of the synthermal. The advantage of the aneroid is its range, and the smaller amount of material usually required. But organic liquid, used instead of water with the solid, diminishes evaporation, increases the range, lessens (on account of its relatively very low heat capacity) the amount of dead heat capacity, and allows working with material soluble in water.

Twins with Duplicate Chemical Heating

L. T. Fairhall and A. B. Lamb [20] have used T. W. Richards' method of chemical heating in twin calorimeters, not to compare the heats themselves, but as a substitute for the accurately equal pair of electric heat

[20] Thesis, Harvard University (1917).

quantities. The complications of batteries, leads, and possible disturbing leakage currents are thus avoided, but the calorimeter is more encumbered, and more time is required, than with electric heating.[21]

Section 19. The Cold Calorimeter

The chief advantage of the twin calorimeter, precision in the thermel reading, is partly obtained if a thermel runs from the calorimeter to a body at about the same mean temperature, so jacketed in a thermostat as to be very constant. Gradients and potentiometer readings are thereby diminished, tho not to zero, yet most of the way, and the attention required by ice baths is avoided. A method of measurement by which the slight variations in the temperature of this body, the "cold calorimeter," are taken care of with very few additional observations, has been described.[22]

Improved Cold Calorimeter

Dr. Barry and I have devised an apparent improvement on this scheme. (1) The cold calorimeter is inside another which is in a thermostat. Changes are therefore slower, smaller, and more subject to control. (2) The thermel from the working calorimeter runs to the outer of the two vessels in the thermostat, and another, in series with it electrically, runs from that to the inner. Hence the temperature of the inner is not affected by even the slightest conduction from the outer air, nor by replacing the main thermel. Since the thermal head of the inner vessel should be read with maximum precision the thermel in it would be needed anyway, and since there is never any gradient on that thermel greater than a few thousandths of a degree, it can, if desirable, be made with inferior selections of wire, with no loss whatever in precision. Emerging stirrer rods and all complication of stirring can be avoided by using metal blocks for the calorimeters, with some, not serious, increase in thermal leakage rate.

Efficiency of the Cascade Cold Calorimeter. If the leakage modulus of each calorimeter is 0.002, which is large, since at least one vacuum-walled vessel can be used, and if adjustments are made once an hour, the inner vessel will be constant to 0.000 03° if its mean thermal head is constant to 0.000 3° after being adjusted. And the mean temperature of the outer vessel will be constant to that even if the thermostat changes suddenly immediately after the adjustment, if the change is not over 0.005°. This result is proportional to the square of the time.

[21] Richards and Gucker, *op. cit.*, p. 1877.
[22] White, Walter P., *J. Am. Chem. Soc.*, 36, 2319 (1914).

For a 30″ interval the thermostat can jump 0.02°. The inner vessel certainly ought to have a modulus less than half 0.002, promising a constancy better than 0.000 015°. This concerns the excellence of the thermostat. If the thermostat is good to 0.001°, as it often may be, with half-hourly adjustments the drift chargeable to it may evidently be made less than a millionth of a degree per hour.

The precision of the cascade cold calorimeter, then, is really limited by the excellence of the hourly adjustments. To get a definite picture of these, we may consider one of the simplest and best of several possible methods of operation. This is to set the thermostat so that the outer cold calorimeter will tend to cool, surely, but very slowly. At each adjustment this calorimeter is heated a known, but exceedingly small, amount by passing current thru its heater for an appropriate small number of seconds, so that the average thermal head of the inner calorimeter is zero for the whole time. This adjustment will be guided by the thermel running from inner to outer calorimeter. This thermel is also read in series with the main thermel running to the working calorimeter, in order to measure the temperature of this against the inner cold calorimeter, hence it is at least as sensitive as the main thermel. If the error of a reading is ε degrees, then if the leakage modulus of the inner cold calorimeter is 0.001 the maximum drift due to that error in 10 hours will be $10 \times 60 \times 0.001\ \varepsilon$, or $0.6\ \varepsilon$. This is less than the error of reading. Ordinarily the drift error will be much less than that.

For time intervals up to two or three days, therefore, the performance of the cascade cold calorimeter, as long as it is watched, should be perfect. For the vast majority of calorimetric experiments, which are short, no attention should be needed after the preliminary adjustment.

Section 20. Calibration, and Electric Methods *

The desirability of experimental calibration, making the calorimeter a transfer instrument, has probably been sufficiently shown already. It arises (1) from the difficulty of computing accurately the heat capacity of various parts and accessories of a calorimeter, and (2) because lags and various other factors may modify the effective capacity. The same fact may be expressed by saying that an experimental calibration eliminates numerous constant errors. It even may correct for thermometric error.

The determination of any known heat quantity may serve as a calibration. In specific heat work, for instance, the measurement of

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the specific heat of a reproducible substance, calcite, has been used as a calibration, while combustion calorimeters are nearly always calibrated by burning samples of benzoic acid or other standard material. It has even been possible to re-calibrate (or correct for systematic error) a set of results after the author's death where the set included typical determinations on reproducible material. Indeed, it is well to have any important series of determinations include one or more substances which can easily be duplicated by other experimenters. Systematic errors or systematic discrepancies between different workers may thus be brought to light, and the best calibrations, past or future, connected with any work on the common material ultimately made available for all.

The greater the similarity between the calibration and the other experiments the greater is the elimination of systematic errors. This elimination may even extend beyond the calorimeter into the associated manipulations and measurements.

In general, however, the errors in the associated measurements will be greater than those in the calorimeter, so that a calibration involving such measurements, tho it may be the best for that particular kind of experiment, is likely to be a poor calibration of the calorimeter itself. Hence in spite of the advantages of similarity between calibration and application it will often be desirable to calibrate also with associated measurements of negligible error, and this will often be necessary thru the lack of appropriately standardized materials.

Special Methods of Calibration

Two methods, on account of the precision attainable in the associated measurements, seem specially suited for calibration of the calorimeter. These are neutralization of acid and alkali, and electric heating.

Neutralization

Neutralization, for many experimenters, will require less special knowledge and apparatus. It can be made to proceed at any rate the experimenter chooses, so that errors connected with the form or determination of the temperature rise curve can sometimes be better dealt with. For those planning thermochemical work a thermochemical calibration of course may have the advantages of similarity. It requires bringing the reacting solutions to temperature, mixing and stirring. Suitable apparatus is described by MacInnes and Braham and by Richards and Rowe,[22a] who also give the temperature coefficient of a

[22a] MacInnes, D. A., and Braham, J. M., *op. cit.*; Richards, Theodore W., and Rowe, Allan W., *Proc. Amer. Acad.*, 43, 475 (1908), *ibid.*, 49, 173 (1913); or *Zeits. physik. Chem.*, 64, 187 (1908), *ibid.*, 84, 585 (1913) (temp. coeff. page 603); *J. Am. Chem. Soc.*, 42, 1621 (1920), *ibid.*, 43, 794 (1921), 44, 687 (1922); with Burgess, L. L., *ibid.*, 32, 1176 (1910).

convenient combination of chemicals. This method of calibration may be made very accurate for comparisons. Its absolute accuracy is dependent on experiments where the heat given has been compared with some more ultimate standard, as by electric heating. At the present writing, therefore (1927), it is less accurate than electric calibration itself at its best, but this deficiency will doubtless decrease as the years go by.

Calibration by Electric Heating

Electric calibration is not only of paramount accuracy, but, on account of the smallness of the modification in the calorimeter needed for inserting an electric heater, it is a favorite method for all grades of precision. With a stop watch and a commercial ammeter or voltmeter it is easy and convenient for 3 per mille average error. Higher accuracy is generally sought by Jaeger and von Steinwehr's [23] method, using a chronograph and a potentiometer. If more than a little work is to be done it is very advantageous to substitute for the chronograph a device whereby the precision clock turns the current off and on.[24] The associated manipulation consists of 6 motions, against 2 where the current is started and stopped entirely by a hand-operated switch, but the care, oversight, and reading of the chronograph are avoided, and the interval is always an integral number of seconds.

Electric Set-up. The electric connections are conveniently arranged as in Figure 9, which differs from arrangements given by other experimenters only in having the equipotential leakage shield, *SH*,[25] which insures that current leaking across the heater shall not go thru the measuring coil.

The coil A serves to measure the current, by means of the voltage drop E_A thru it. Similarly B measures the voltage drop in the heater, which is evidently

$$E_B \frac{R_C + R_B}{R_B}. \quad R \text{ signifying resistance.}$$

C is a relatively high adjustable resistance. If it is so set that the voltage drops thru A and B are equal, both of these can be measured on the same potentiometer setting, which promotes speed. In that case, also $\frac{R_H}{R_C + R_B} = \frac{R_A}{R_B - R_A}$, or R_H is to R_C approximately as R_A is to R_B.

[23] Jaeger, W., und v. Steinwehr, H., "Eichung eines Berthelotschen Verbrennungskalorimeters in elektrischen Einheiten mittels des Platinthermometers," *Ann Phys.*, **21**, 49 (1906).

[24] White, Walter P., *Phys. Rev.*, **31**, 688 (1910). This is a development of a method of Dr. N. E. Dorsey's. Ingenious automatic methods pertaining to the making of chronograph records are found in the preceding reference and in Dickinson, H. C., *U. S. Bur. Standards Bull.*, **11**, 225 (1914).

[25] White, Walter P., *Phys. Rev.*, **31**, 687 (1910); *J. Am. Chem. Soc.*, **36**, 2015 (1914).

In any case the current thru H, I_H, is given as $\frac{E_A}{R_A} - \frac{E_B}{R_B}$. The leads in the shunt circuit with B and C will usually be negligible in comparison to R_C, but can always be measured and counted as part of it.

Error of Averaging. The readings of E_A and E_B will usually vary perceptibly during even a heating of 2 minutes, and the simplest way to

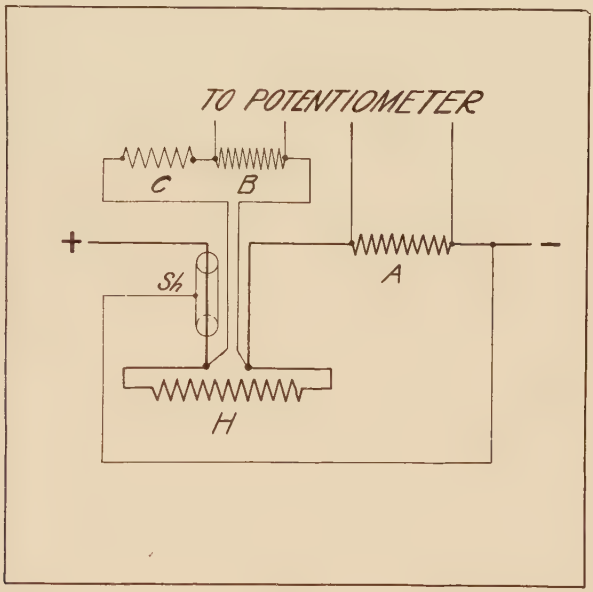

FIG. 9.—Diagram of connections for measurement in electric heating. H, heater; A, current measuring coil; B, voltage measuring coil; C, appropriate high resistance; Sh, equipotential leakage shield. (It should cover the positive potential lead also.)

treat them is to average them. But when the current and the voltage both vary in the same sense, an error arises as follows: The energy, and therefore the heat, is proportional to $\int_0^T E_H I_H \, dt$, while averaging gives $(\int E_H dt) \times (\int I_H dt)$, which is not the same. Calculation, however, indicates that the difficulty of reading a variable voltage would usually set a limit to precision before the variation was great enough to make averaging inadmissible.

Precision Required. It is decidedly troublesome to exceed an accuracy of 30 per million in the electric power measurements. Hence it is fortunate that this accuracy is ideally sufficient for the highest calorimetric accuracy, 0.3 per mille, which has yet been reported, and

not incompatible with the highest, 0.1 per mille, which it seems worth while even to consider. In many cases, also, if the electric performance is consistent enough to test the *precision* of the calorimeter, a somewhat lower *accuracy* is sufficient.

There are, however, two ways in which precision may be jeopardized, even with adequate standard coils and a steady storage battery.

Lead Errors with Low Voltage. The discussion given here of errors connected with the leads applies chiefly to batteries with a voltage of 100 or over. In many cases, however, the experimenter will not have available the number of cells required to give this voltage, and will have to make up for the lack by using a relatively large current. This will increase the heat produced in the leads, which for 10 volts will be 100 times what it would be for 100 volts. If the leads are made larger to avoid this difficulty the ordinary conduction of heat will be seriously increased. No doubt a compromise will generally be best, but for high precision with lower voltages the leads, and especially their thermal contact with jacket and calorimeter, will need much more study and care than has generally been given to them.

Poor Contacts. Another detriment to precision is imperfect switchboard and rheostat contacts in the battery circuit. Altho the error from such varies inversely as the voltage, it is likely to be perceptible even at 110 volts. The experimenter who, from the heater away back to the battery, eliminates unsoldered contacts as far as possible, and makes clean and firm those that are left, may be much surprised at the increased precision of his results, arising from greater steadiness of his battery current.

Timing Precision. A desirable time for the electric heating will often be not over 3 minutes in precision work. Then for precision of 30 per million the timing error of both beginning and ending must not exceed 1/150 of a second, or 0.003″ for each, and a smaller value, say 0.001″, is of course desirable. If the uncertainty of the position of effective contact by the switch is taken to be 2 mm., then in Dickinson's method of recording the time of contact, or in the Dorsey method of turning on by the clock, the speed of the switch at contact should be $0.2 \div 0.003$, that is, 67 cm. per second, or better. This is not hard to get, but may not be reached by experimenters who have not determined what their speed is. The measurement is very easily made. The switch is arranged so as to move horizontally, and to carry a small object which is free to continue moving when the switch stops. The vertical and horizontal distances to the point where this object strikes the floor or table then enable the velocity of projection, which is the

maximum velocity of the switch, to be calculated by the laws of falling bodies.[26]

Management of the Observations [27]

A second observer, with complete apparatus, can take care of the electric energy readings, including the time, so that the calorimeter can be observed as usual. A single practised observer, with good apparatus, can also do all the work alone if the calorimeter temperature is read electrically; most simply if a potentiometer can be used for all the measurements. A superior method, however, for fluid-filled calorimeters and heatings not over 5 minutes long, is to calculate the average calorimeter temperature during the heating, by means of observations made immediately before and after. It evidently makes the second observer quite superfluous, and enables a single one to give more complete attention to the energy readings. It therefore seems to deserve examination.

Indirect Method for Finding the Thermal Head. The conditions on which the calculation method has to be based are as follows:

It will be convenient to treat first the case where the thermal head is practically zero at the beginning of the heating. If OA in Figure 10 represents the course of the calorimeter temperature before the heat is turned on at the time of A, for the time $T, = AB'$, then ABM may represent the temperature corresponding to the energy which has been given to the calorimeter. The temperature read is caused to vary from this simple scheme by two things, first the lag, and then the thermal leakage. The lag alone would make the temperature follow the line $AEFG$, which, if the lag is not unusually large, may with quite negligible error be taken as coincident between two points, E and F, with a line CD, parallel to AB, and at a point G with BM. Then the horizontal distance $AC, = BD$, represents the time L_H, the lag of the calorimeter temperature behind the energy supply. The shaded areas ACE and FDG are equivalent, hence the mean temperature and consequently the mean thermal head will be just the same if the line followed is $ACDM$, and this will be taken as the result of the heating.

This temperature pattern is further modified by the thermal leakage which it itself causes. The modification is merely a fall of temperature

[26] In our clock-operated switches the contact is made by a rod striking a plate, so as to give the maximum definiteness in time of contact. But a study of various times connected with the operation of the switch, made with a ballistic galvanometer, has showed that the rebound of rod and plate after first striking gives an effective interruption of the current as long sometimes as 0.01 second. An uncertainty of 2 mm. in place of contact, on the other hand, produces an error which is quite negligible. Hence it is decidedly preferable to make the contact by a knife switch rather than by a plate.

[27] The rest of this section is reprinted, with slight alterations, from *J. Wash. Academy*, **13**, 17 (1923).

everywhere proportional to the actual thermal head, and giving that when superposed on the pattern *ACDM*.

For calculating this, the only measurements needed during the calibration are two, of calorimeter temperature or thermal head, one before the heat is started, the other long enough after its end to allow the difference between the converging lines *DG* and *FG* to become negli-

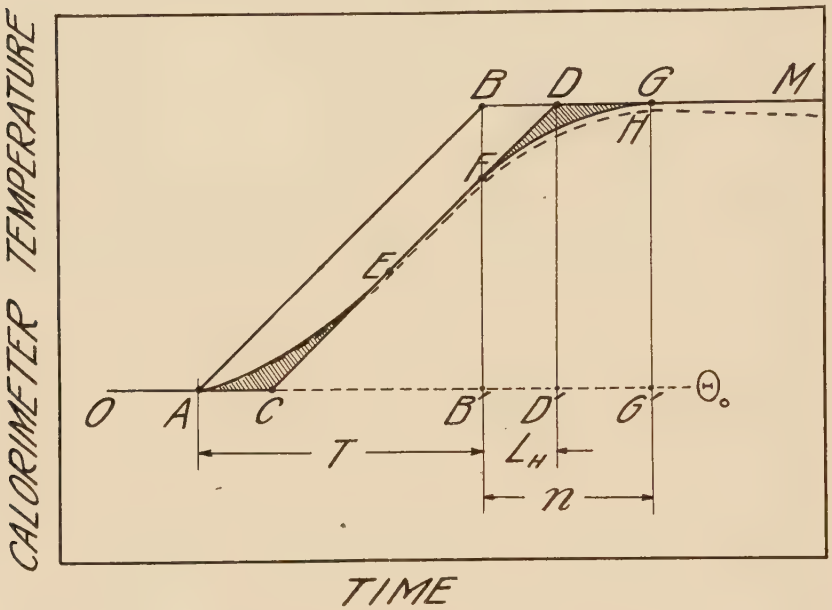

FIG. 10.—Temperature pattern of electric heating, accompanying the derivation of a new method of determining the thermal head.

gible. These data may then be used in accordance with the result of the following demonstration:

If q is the temperature rise corresponding to the heat supplied per minute, A the jacket temperature, and K the leakage modulus,[28] the temperature, neglecting lags, is easily shown to be:

$$\theta = \frac{q}{K} + A + \left(\theta_o - \frac{q}{K} - A\right) e^{-Kt} \qquad (35)$$

It will be convenient to write the exponential as a series, giving:

$$\theta = \theta_o + \left\{q - (\theta_o - A)K\right\} t \left(1 - \frac{Kt}{2} + \frac{K^2t^2}{6} - + \right) \qquad (36)$$

[28] Thermal leakage modulus, temperature fall per minute per degree of thermal head. Thermal head, mean effective temperature difference between calorimeter surface and surroundings.

$\theta_o - A$ is O in the present case. Since this expression for calorimeter temperature is to be multiplied by K to get the temperature change due to thermal leakage, then for water-filled calorimeters, where K is seldom much over 0.003, the terms now containing K^2 and higher powers will contain a factor of $0.000\,000\,027\ t^3$ or less, and may be neglected unless t is uncommonly large. Similarly other terms containing K^2 will be omitted later. The physical meaning of the omission is this: In defining the temperature pattern, which is to be multiplied afterward by the very small factor KT, we will take account of the change in temperature due to the leakage produced by the impressed temperature, but find negligibly small the change in the leakage caused by the temperature change due to the leakage.

If n denotes the time from the end of the heating to the first direct thermal head measurement afterward, represented by BG, then the time from D to G is $n - L_H$. Thermal head is the same as the temperature rise above θ_o since it was taken as zero for $\theta = \theta_o$. On account of thermal leakage, the temperature after $T + L_H$ minutes is not $D'D$ which equals qT but, by (36) $qT - qt\frac{KT}{2}$; and after $n - L_H$ minutes more is still lower, or, say, $G'H$. This is the temperature actually observed. Then the *true* integrated thermal head, $\varphi T'$, to the time of G is the head during the temperature rise plus that during the approach of equilibrium, or:

$$\varphi T' = \int_o^T \left(qt - qt\,\frac{Kt}{2}\right) dt + \left[qT - \frac{qKT^2}{2}\right] \int_o^{n-L} (1 - Kt)\,dt$$

which gives for the true integrated thermal head for the interval $T + n$:

$$\varphi T' = qT\left\{\frac{T}{2} - \frac{KT^2}{6} + (n - L) - \frac{KT}{2}(n - L) - \frac{K}{2}(n - L)^2\right\} \quad (37)$$

with a term containing K^2 omitted. For *calculating* an *equivalent to this* the temperatures at times A and G' in the figure are given. It is then a method which sufficiently combines accuracy and convenience to assume that the temperature, starting after an interval of L_H minutes from A, rose at a uniform rate for T minutes to the temperature $G'H$, and then remained constant at that temperature for $n - L$ minutes. That is, the temperature rise is simply multiplied by $\frac{1}{2}T + n - L$. Now the temperature at H actually is, in accordance with (36):

$$qT\left(1 - \frac{KT}{2}\right)\left(1 - K(n - L)\right) \quad (38)$$

Hence, using the approximation just suggested, the calculated thermal head is:

$$\varphi''T' = qT\left(1 - \frac{KT}{2}\right)\left\{1 - K(n-L)\right\}\left(\frac{T}{2} + n - L\right)$$

which is, again omitting terms containing K^2:

$$\varphi''T' = qT\left\{\frac{T}{2} - \frac{KT^2}{4} + (n-L) - KT(n-L) - K(n-L)^2\right\} \quad (39)$$

The difference between this and (37) is the error of the approximation made in calculating. It is:

$$\delta(\varphi T') = qTK\left\{\frac{T^2}{12} + \frac{T(n-L)}{2} + \frac{(n-L)^2}{2}\right\} \quad (40)$$

The calculated thermal head is too small by this amount. A glance at (37) shows that this error is over half of the real change in $\varphi T'$ due to the leakage.

With $T = 4$, $n - L = 1$, $K = 0.003$, this error causes a final error of 0.000,036 qT, which is safely negligible even in work of 0.1 per mille precision, but can also be corrected for with ease. $n - L$ should usually be less than half a minute. With the large values of K characteristic of some aneroid calorimeters, closer approximations would be needed.

The understanding of (40) and the application of it may be facilitated by a glance at its physical interpretation. If in Fig. 10 we take the equivalent temperature path $ACDGM$ as the one that would have occurred in the absence of thermal leakage, then the peak of the actual path occurs at the time D', and from that peak there is a slight drop to H, equal to $K\Delta\Theta(n - L)$, or $KqT(n - L)$. But the approximation suggested puts the peak of the path no higher than H. It therefore cuts off two triangular areas that are under the actual curve, whose height is $KqT(n - L)$, and whose bases are T and $n - L$. These form the second and third terms in (40). The first term, as its origin shows, arises because the approximation takes the rise as linear, whereas it is curved, owing to the fact that the thermal leakage along it increases from 0 to KqT with the increase of the temperature from 0 to qT.

In using this method the value of L, the lag represented by BD in Figure 10, should be known rather accurately, since this affects directly the time assigned to the higher temperature, and so is in effect multiplied by $K\Delta\Theta$ in getting the thermal leakage. Hence for 0.01 per mille precision, that is, for security in 0.1 per mille precision, L, if K is 0.003, should be known to 0.003 minute, or .2 second (Equation 4), like any other lag affecting the whole calorimeter. A very satisfactory way to determine it is this: Make a series of blank heatings, observing

only thermal head or calorimeter temperature, as frequently as, say, every 15 seconds. Then, as in any regular calorimetric determination, find, from the calorimeter temperature, the total heat supplied, and also find the temperature loss up to the time of each 15-second reading, which is not nearly so troublesome as it may sound. Then, knowing the total heat, the fact that it was supplied uniformly, and the temperature losses, compute the calorimeter temperature corresponding to the heat actually in the calorimeter at each reading. Comparing these with the observed temperatures gives a series of values for the lag, whose average is comparatively unaffected by the fluctuations of the rapidly rising temperature, and of course has the thermal leakage eliminated. The same data give a check of correction (40) for the apparatus and conditions employed. The total leakage is usually so small that a predetermined value of K is quite good enough, hence no rating periods ("after periods") are needed. In a number of tests of this procedure the check of (40) was seldom out by more than one-third of (40) which, in this case, was about the uncertainty of a single reading, and corresponded to 0.25 second during the rapid rise of temperature. The main probable cause for the discrepancies observed was the fluctuation of the rising temperature as read. This seems to show that where the lag is constant the method of calculation here given, corrected by means of (40), will probably give more accurate results in actual calibrations than observations of φ. Readings once a minute, however, though less accurate, will, with reasonably good stirring, be sufficient for observing the thermal head; this is why it can be observed along with the electric energy.

Such readings may be preferable or even necessary if the blank heatings have shown the lag to be variable.

Blank heatings will also enable an empirical expression, a substitute for (40), to be found in cases where the lag is large, and where, consequently, the two triangular areas are not independent of each other, and (40) does not hold. Indeed, blank heatings alone might be used in most cases. The preceding analysis, however, seems generally useful in giving an idea of the sources of error, and of the precautions that must be taken if there is an initial thermal head, or if the jacket temperature changes, matters whose purely empirical investigation will generally be very tedious and of inferior accuracy.

Extension for Initial Thermal Head. An initial thermal head, that is, a difference between calorimeter and jacket at the time, A, will cause a thermal leakage which will be simply added to the one already considered, due to the heating. This leakage may properly be taken as

modifying the initial thermal head which causes it, but as having no other effect. The two thermal heads, each with its resultant leakage, may therefore be considered as separate. The measurement made at the time of H in Figure 10 takes them together. A separate and additional correction, however, similar to (40), can be made for the additional error of the approximation of (39) when φ_o is not zero. For this it is sufficient to note that the drop from the peak to H has an additional component, $K\varphi_o(n - L)$, and that there is a drop, $K\varphi_o L$, from A to C. Hence we have to add the triangular areas $-\frac{KL^2\varphi_o}{2}$ and $+\frac{K(n-L)^2\varphi_o}{2}$, while the area under CD is increased by $K\varphi_o(-L+n-L)\frac{T}{2}$. The sum of these three terms is:

$$K\varphi_o\left(\frac{n}{2} - L\right)(n + T), \tag{41}$$

which is to be added to (40).

Change in jacket temperature can be similarly treated. If the jacket is electrically heated, so as to give a nearly adiabatic method, its lag, as usually in adiabatic work, will be as important as the lag in the calorimeter.

Initial Change in Heating. When the current is first turned into the heater the resulting change of temperature of the wire will generally cause an initial change of resistance and the value for the first few seconds will be different from that measured. If the resistance for the first 10 seconds of 3 minutes differs by 1 per mille from the later, measured value, the discrepancy is appreciable in work of 0.1 per mille precision. Changes greater than this are possible, even in constantan wire, if the attempt is made to run at anything like the highest safe temperature. Although difficult to follow during a regular run, the change can easily be measured, and should be, by special experiments where nothing else is attempted, but subsequent variations in it will of course cause error. Unlike the lag effect already discussed, it has no tendency to cancel itself, since the reverse change in resistance comes only after the current has ceased to flow. To keep the heater coil running at a low temperature diminishes this error, and also that from loss of heat along the leads.

Dealing with Unsteady Batteries

Unsteady batteries are scarcely compatible with the very highest precision; with them the best results are obtained by some departure from standard procedure. (1) Very frequent, uninterrupted measure-

ments of current or voltage tend to diminish the error from irregularly varying voltage, but demand either two observers with complete sets of apparatus, or else reliance upon the constancy of values for coil resistance, correlated with current and calorimeter temperature, determined by separate special experiments. (2) The voltameter, giving directly the product of current and time, handles perfectly the most sudden and irregular fluctuations [29] of current, and still leaves the observer's time free for other things. This time can be employed for measuring the coil resistance by a Wheatstone bridge, using the heating current itself as the bridge current.[30] This involves a loss of simplicity in the electric circuit, but is of advantage if it is desired to shunt part of the current by the heater, in order to give the voltameter the relatively large current which promotes accuracy with it; the Wheatstone bridge measurements can also be used as measurements of the shunt ratio. A further disadvantage is the relatively long time, 20 minutes at the very least, needed for high precision with the voltameter.

Errors Connected with the Leads

The proper place to put the potential terminals, whose location determines the amount of heat that comes into the measurement, is not at the ends of the constantan wire,[31] but outside the calorimeter altogether, at a point such that the heat generated in the lead wire between it and the calorimeter equals that flowing from the wire to the calorimeter. In general, the accurate location of this point is rather difficult, but it becomes easy if the heat given to the air can be neglected, since the proper point is then simply the middle of the free portion of the leads.

Loss to the Air. The heat given to the air is easily found to be:

$$QX - \frac{Q}{\mu} \tanh \mu X \qquad (42)$$

where Q is the heat generated in each centimeter of the wire, $2X$ is the length of each lead between surfaces, and the parameter $\mu = \sqrt{\frac{EP}{AK}}$, where E is emissivity, K thermal conductivity, A area, P perimeter. Langmuir's stationary surface layer rule has been used to

[29] There is evidently an error from very large fluctuations, owing to the fact that the heat is as the square of the current, but this error is usually quite negligible, and if not, can be avoided by a little coarse voltage regulation. The voltameter result is also sufficient when accompanied only by *accurate* measurements of voltage. In this case the voltameter makes the time measurement unnecessary, but does not deal well with voltage fluctuations.

[30] This has been done; the reference is not at hand. The coil resistance will vary very much less than the current, hence is far more easily measured when the current is unsteady.

[31] *See* Dickinson, H. C., "Combustion calorimetry and the heats of combustion of . . . ." *U. S. Bur. Standards Bull.* **11**, 222 (1914).

get E.[32] Relatively crude data are here sufficient, since the attempt is only to determine when certain quantities are negligible, not to compute appreciable corrections.

One ampere at 110 volts generates 4733 calories in 3 minutes. In 1 cm. of No. 24 lead wire (about 0.5 mm. in diameter) it would generate 0.03626 calories, which number can conveniently be doubled, since we are dealing with a pair of leads, so the heat is 0.073 calories per cm. of lead length. For this wire, μ, calculated as in Section 9, may be taken as 0.28, and 0.51 for No. 30 wire, while 0.16 was given for No. 18. We then have the values in Table VI for heat given to the air and not delivered at the ends, in 3 minutes.

It thus appears that, when the voltage across coil terminals is 110, and the current 1 ampere, with No. 30 leads 4 cm. long, No. 24 leads 10 cm. long, and No. 18 leads 28 cm. long, the heat lost to the air from the leads may be simply neglected. This is true even if the potential leads increase the loss to the air, which they will scarcely do if wound helically on the others and cemented there by shellacking. Moreover, the heat that goes into the air will in part return to the calorimeter, so the final loss is less than given in the table. On the other hand, the wire will not take the calorimeter temperature just at the surface, and the point of mean effective contact may be 1 or 2 cm. within. This will make the air loss as great as if part of the extra length were added to the wire in air, so it will be safer, in applying Table VI, to take 2X as 2 cm. more than the free length of the wire.

TABLE VI.—Approximate Loss to the Air, in Calories, in 3 Minutes from Half of 2 Lead Wires of Length 2X Each.

	X, cm.	Diameter, mm.		
		1	0.5	0.25
1 ampere	1	0.00016	0.0018	0.023
	2	.0012	.014	.14
	3	.0039	.04	.35
	4	.0086	.08	
	5	.016	.13	
	10			
	14	.14		
5 amperes	1			0.57
	2.5		0.62	
	6.5	0.75		
5 amperes	0.5			0.14
	1.5		0.15	
	3.5	0.148		

[32] *See* White, Walter P., "The conditions of calorimetric precision," *J. Am. Chem. Soc.*, **40**, 1882 (1918).

The bottom section of the table gives combinations of wire diameter and length whose loss to the air is about 30 per million of the heat generated in a heater of 4.4 ohms, *i.e.* one carrying 5 amperes at 22 volts. The middle section gives similar combinations for a heater of 22 ohms, the upper one includes such for a heater of 110 ohms. Thirty per million is a negligible error for 0.3 per mille precision, but, being systematic here, may be classed with errors negligible for 0.1 per mille also.

Thermal Contact Error. Of more importance may be the effect of the uncertain contact on the flow of the heat that does not go into the air. If the contacts are symmetrical no error results; if one is effectively 1 cm. deeper than the other, that is equivalent to a displacement of 0.5 cm. in the potential lead attachment. This, for 1 ampere, 110 volts, gives a systematic error of about 8 per million of the total heat with No. 24, and of only 30 per million even with No. 30 leads.

Size of Wire. Thus with a little care even No. 30 wire will usually make satisfactory leads for a heater that can raise a liter calorimeter 5° in an appropriately short time. Coiled leads of larger wire are safer, but less convenient. Direct leads of larger wire increase various undesirable leakages unnecessarily.[33] If 5 amperes is used the heat produced in the wires is 25 times as great, but at 110 volts the allowable heat leakage is 5 times as great; not so if the 5 amperes is used to give the same heat, at lower voltage. The limits of tolerance of air loss for each case are shown in the second and third sections of Table 1. For a given size of wire the proportional error is constant for a given coil resistance, regardless of current or voltage. The error from lack of symmetry in the thermal contacts at the two ends of the free portion of the leads may also become serious. For 1 cm. difference, 5 amperes and 110 volts, this error is nearly 40 per million for No. 24 wire, which therefore seems the very smallest that should be used as leads for 100 per million precision with coils of as low resistance, 22 ohms, as is required *for this current and voltage.* Another advantage in using slender leads is that they can be removed from the calorimeter with but little change in the total heat capacity. This is assuming that the heater itself remains, so that any uncertainty there may be as to its heat capacity does not affect the application of the result of the calibration.

The conductivity of the potential leads may disturb the symmetrical distribution of the heat generated in the current leads. This can be avoided by making the potential leads symmetrical with respect to calorimeter and jacket, as by having one lead run from the neutral

[33] Including possibly the leakage from the room thru the jacket (Section 9).

point into the calorimeter, there turning around (still insulated electrically) to run entirely across the gap and out through the jacket.

Temperature of the Heater Case. Thus far the upper part of the heater case and the leads within it have been taken as at the calorimeter temperature, except for a slight correction due to the effect of heat coming in from the free part of the leads. If the upper part of the case or the leads are heated above the calorimeter temperature by the heating coil itself, the only way of avoiding an uncertain correction appears to be to run the leads a sufficient distance in close contact with some conducting body which, by immersion in the water or attachment to the calorimeter wall, or in some other way, is kept at the calorimeter temperature. If only the leads are heated and not the top of the case, it may be sufficient merely to have the leads run a considerable distance before leaving the case.

The required distances can be calculated by the formulas of Section 9. For example, the following results were thus obtained for No. 24 wire, running 5 cm. in the case and 6 cm. through the air to the jacket. For this wire μ in air has been taken as 0.28. For the wire in close thermal contact with a plate on one side only, as it would be if wound around a central mica strip in a flat case, μ can be taken as 1.7. Then if θ_0 is the temperature of the inner end, next the heater coil, of the 5 cm. of wire, referred to the calorimeter-air-jacket temperature as zero, the temperature where the wire enters the air is $0.08\,\theta_0$, and the heat carried away by 2 leads in 3 minutes is $0.0164\,\theta_0$ calories. For 110 volts and 1 ampere the systematic error of such an arrangement with the heating coil running at 120° would be about 1 per mille, and the coil must heat less than 3° to safely avoid systematic error in work of 0.1 per mille precision. By doubling the length of lead in the inclosure the permissible heating is increased, somewhere near 8 times. A doubling of μ would have an identical effect, but would be rather hard to secure with the same size of wire. It therefore seems that it would generally be very desirable to insert portions of finer lead wire next the coil, using enough larger wire further out, but well within the calorimeter, to dissipate to the calorimeter the heat generated in the fine wire. Advantageous dimensions can be calculated from the data already given. The insertion of too much copper resistance gives the total heater resistance too great a temperature coefficient.

The assumption of temperature equality between calorimeter and jacket, used in this section, is justified as follows: The temperature distributions and flows existing at any time are the resultant of the electric heat and of the jacket-calorimeter difference, and may be

resolved into components due to these different sources. Since by a well known principle the resultants of such components can be obtained by simple addition, and since the results of the calorimeter-jacket difference are taken care of in the regular procedure, we may treat the electric effects alone, as if the others were non-existent.

Chapter V

Particular Apparatus

Section 21. General Construction

Covers

Except in the case of some special procedures, such as the collection of gases, the chief object in covering a calorimeter is to prevent evaporation. The requirements are two: sufficient tightness, and the absence of any lag which may cause errors. Lag may be practically eliminated by having a goodly part of the metallic cover, or else some well-conducting projections from it, come in contact with the circulating water. Such contact is very seldom difficult, and should be provided almost universally, since conveying heat through the calorimeter wall is less effective at best, and is often quite insufficient.

In calorimeters of ordinary size even a very thin cover, if of a good heat conductor, as copper, will ultimately receive much more heat by conduction from the calorimeter rim than thru the air space from the water, and metallic conduction will still more preponderate if connection with the water, other than the rim, is provided. There is thus a loss of efficiency as the material of the cover becomes poorer conducting, and no offset to this disadvantage has been pointed out. If the conducting cover is thicker it will be nearer the temperature of the calorimeter water, tho a very good connection with the water will be necessary to avoid considerable lag. The thicker cover should give a more constant value of K from day to day, since conduction across the air space, which includes some evaporation, has less to do with its temperature. There is doubtless an optimum thickness, tho a moderate divergence from it can hardly be much of a disadvantage. A very thin cover will be safer, since by **(L 15)** the chief error varies with the heat capacity of the cover. A copper cover 10 cm. in diameter and 0.1 mm. thick has a capacity 0.64 per mille of that of a liter calorimeter. If receiving heat only thru the air space, and if 1 cm. from water surface and from jacket cover, its effective capacity, by **(L 15)** page 95, is only 0.16 per mille, and the variation of this capacity, the important thing, is (as can easily be shown by a formula similar to **(44)**) only 0.013 per mille of

the whole for a shift of 1 mm. in the water surface, and only 0.04 per mille for a complete suppression of evaporation. These slight errors will be further diminished by the conduction along the metal, and will become less as more of the cover is brought into direct contact with the water.

The behavior of covers of any thickness can very easily be observed, in as much detail as is desired, by soldering thermocouples to them. The crudest of *calorimeters* will do for the test.

Sealing Around the Stirrer Rod. There are several ways of sealing around the stirrer. Dickinson used simply a small greased washer over a hole slightly larger than the shaft. I have used and described [1]

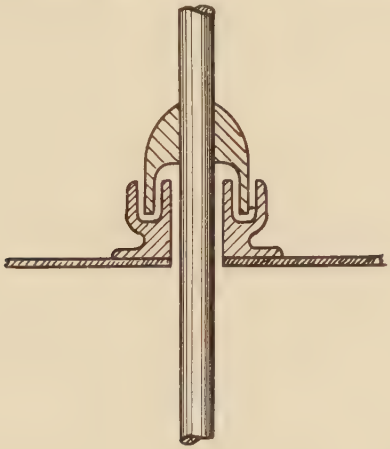

FIG. 11.—Evaporation seal around a stirrer rod. Oil is usually put in the groove.

two forms of oil seal (Figs. 11 and 12). These seem almost ideally efficient, tho perhaps needlessly elaborate. If the oil is omitted the narrow tubular opening restricts evaporation enough for most requirements. Indeed, the dimensions shown in Figure 12 are appropriate to this method; a shorter tube and wider clearances are probably better with oil. A tube running upward would need no cup; the depressed arrangement of Figure 12 makes a long tube compatible with a smaller air gap above the calorimeter.

JACKET COVERS

Of jacket covers, four kinds seem preponderant: The submarine, the water cap, metal covers dipping in water which surrounds the calorimeter, and covers of poorly conducting material, such as wood or rubber. These last do not seem to deserve further discussion.

[1] White, Walter P., *J. Am. Chem. Soc.*, 40, 1888 (1918).

The Submarine. The submarine inclosure of T. W. Richards is in principle the simplest way to surround the calorimeter completely by the jacket water. The calorimeter is inclosed in a case which is immersed in the water, with tubes leading up to the air for thermom-

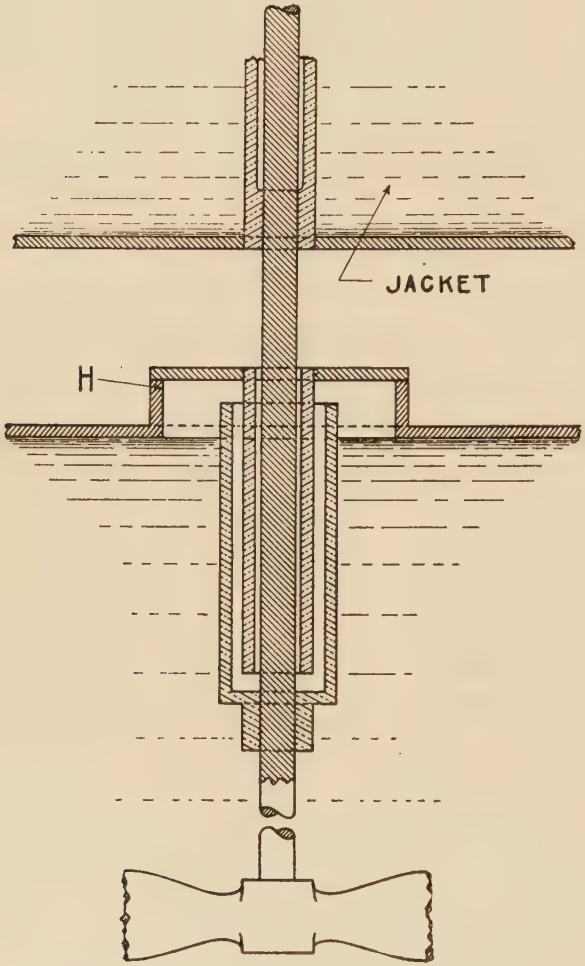

FIG. 12.—Another form of seal, projecting less above the calorimeter.

eter and stirrer. The necessary water-tight seal has been made by gaskets,[2] or by a ground joint [3] (Farrington Daniels). We have made a very imperfect fit tight with stopcock grease,[4] since the water pres-

[2] Richards, T. W., and Jesse, R. H., *J. Am. Chem. Soc.*, 32, 272 (1910).
[3] Daniels, F., *J. Am. Chem. Soc.* 38, 47 (1916).
[4] Suggested by C. M. Shaw, Master Mechanic at the Geophysical Laboratory.

sure on it is only that of a few centimeters. The objections to the submarine are the inaccessibility of the calorimeter when inclosed, and the *relatively* inconvenient setting up.

The Water Cap. These objections may be avoided with our "water cap" cover. This is an inverted U-tube, flattened out in the middle over the calorimeter, with the legs dipping downward into the main body of water, the whole filled by suction with water which is held up by atmospheric pressure. One of the best arrangements of stirring paths is shown in Figure 1. It is evident that the water flows as easily thru the cap as if the free water level were above its top. In order to realize the convenience which this device makes possible, the cap should be movable sideways without emptying it or disturbing the stirring or lifting the thermometer. This can be accomplished as in Figure 1. There are two caps, movable without emptying, and the stirrer and thermometer come up in a narrow space between them. It often does nearly as well to have the stirrer mounted on one half-cap,[5] moving the other to give access to the calorimeter. In an earlier form the two arms of the inverted U were near together, and the single cap rotated about them to uncover the calorimeter. This has been adopted by the Bureau of Standards, and is shown in one of their publications, Scientific Paper 230, p. 212 (1914), Figure 2.

The Metal Cover. A simple jacket cover of sheet copper, not too thick to be cut with heavy shears, is quite sufficient with most calorimeters. The edge of the cover bends down to make good contact with the jacket water (Fig. 13). The efficiency of such covers has been recently discussed.[6] The effective lag is 1 second in non-adiabatic, 10 seconds in adiabatic work, and the temperature uniformity of a blanketed double cover is nearly or quite good enough for 0.1 per mille precision. The protection against leakage of heat along rods or wires is less than with water-filled covers. Over the small tops of Dewar vessels sheet copper jacket covers are especially efficient.

Form of the Calorimeter

The shape of calorimeter which is easiest to make, to cover, and to fit with a jacket is doubtless a cylinder. This shape has also been shown to be easy to stir (page 71).

Height. Altho stirring is often a little more efficient with a calorimeter wider than it is high, there may be preponderant reasons for following the usual custom, and making the height 1½ or even 2 times

[5] Fig. 2; *Phys. Rev.*, 31, 673 (1910).
[6] White, Walter P., *J. Am. Chem. Soc.*, 48, 1149 (1926).

the diameter. This diminishes the convection effect, which becomes less both because the sides are high and because the ends are small (see Section 8); and it also diminishes the slight lag or heat capacity effects due to the calorimeter rim and the cover. With a vacuum-walled calorimeter, where the heat transmission per square centimeter is far

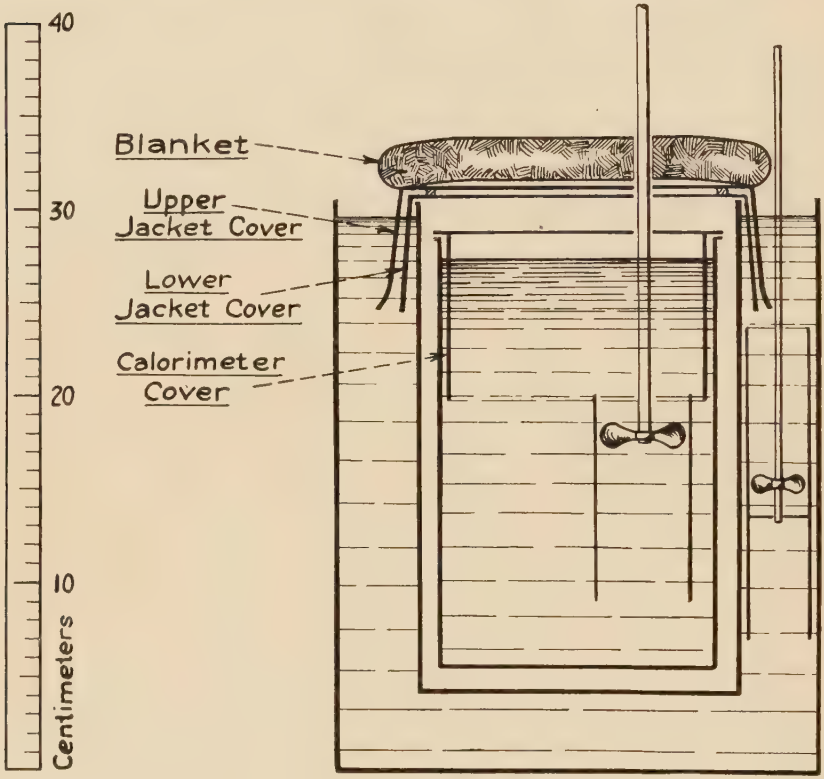

FIG. 13.—Calorimeter jacket cover arrangement, of copper and cotton wool, giving practically perfect exclusion of room temperature influence.

greater at the top than on the sides, it is profitable to carry the lengthening further, and make the height 3 or 4 times the diameter.

The Size of the Calorimeter. If the height and width of a calorimeter are each increased n times, the surface has n^2 times its old value; the volume and heat capacity about n^3 times; the leakage modulus, K, which increases with surface, but diminishes with volume, will be $n^2 \div n^3$ times as large, that is, n times as small as before. The heat capacity of thermometer, supports, and solid materials generally, will be relatively smaller.

If the larger calorimeter is used to measure a correspondingly larger quantity of heat the smaller value of K will be an advantage up to the point where the errors connected with K have become negligible.

If it is a case of measuring the same amount of heat with a larger calorimeter, the greater heat capacity will cause the temperature rise to be only $\frac{1}{n^3}$ times as great, and to measure this with sufficient proportional accuracy will soon become impossible, on account of thermometric errors. But where sufficient thermometric precision can be obtained, it has often been thought that there is a gain in precision by increasing the size of the calorimeter, because of the smaller value of K and the smaller relative heat capacity of the solid parts. My own contention, however, has been that there is usually no such gain. The reasons for this position are as follows: (1) The relatively smaller heat capacity of the solid parts and the smaller lags are usually of little importance in an experimentally calibrated calorimeter. The only serious lag effect, usually, is the internal lag effect, which is a matter of stirring and has been shown to be actually larger (page 72) in a larger calorimeter. (2) In spite of the smaller value of K a given inaccuracy in measuring or controlling the environing temperature causes a larger final error with the large calorimeter, since the flow of heat is proportional to temperature difference and area, and the area is n^2 times as large, while the *external* temperature difference is no smaller. Indeed, it is harder to avoid inaccuracy in the environing temperature as the jacket becomes larger.

Section 22. The Vacuum-Walled Calorimeter

Characteristics

The vacuum-walled calorimeter has the following characteristics:

Heat Insulation. The rate of heat loss may run a little lower than 0.5 calory per minute per degree of thermal head for a liter bottle, corresponding to K[7] $= 0.005$, or about 4 times as small as for an ordinary calorimeter of the same size, but is more likely to be 0.0007, or only twice as small as it can be in other calorimeters with a convection shield, or with the adiabatic method. (See pages 65, 80, 118, 169.) Two-tenths of a loss of 0.5 cal. may be due to conduction thru the glass neck, if this is 5 cm. in diameter and a length of 2 cm. intervenes between water and cover. With a neck 8 cm. in diameter, the largest that would ordinarily be used with a liter vessel, and with 2 cm. intervening above the water, the calculated leakage thru air and glass at the

[7] K, the *thermal leakiness.*

neck is about 0.3 calory per degree, or half of the whole. The conduction thru thermometer, stirrer shaft, heater leads, and similar structures will be more *in proportion* than with calorimeters of larger K, tending to diminish the advantageous ratio of the glass vessel itself.

Lags. There will be a lag of the glass above the water, but the total effective heat capacity of this portion of glass will usually be only 2 per mille, and the effective time for 0.9 equilibrium is only 5 minutes. This value is on the supposition that the glass at the very top of the mouth is at jacket temperature, with 2 cm. intervening.

Heat Capacity. The heat capacity of the solid parts will vary with the depth of water at the rate, usually, of about 1 per mille per cm. difference of level. It therefore appears that this possible variation demands strict attention, but that those who have feared it must always be a serious source of error have exaggerated its difficulties. The water level can easily be kept constant to better than a millimeter (0.1 per mille heat capacity) by Dickinson and George's internal overflow device. If no structures of variable volume are to be put in, the determination of the amount of water ipso facto determines the heat capacity of the wet glass with far greater precision. The expansion of the water in heating 5° changes the effective heat capacity of the wet glass 0.03 per mille of the whole.

Organic Liquids and Heat Capacity. If organic liquid is used to diminish evaporation or electric leakage (see page 106) the relative heat capacity error of the glass wall is increased, 2.5 times with kerosene. Otherwise, organic liquids and the vacuum-walled vessels are well suited to each other, for the non-equalization error, unusually large with such liquids, is more tolerable in the vacuum vessel, while electrically conducting films of condensed water are especially undesirable in it.

Low Cost. The experimenter who purchases a Dewar flask and puts it in a can of water has secured at the same time, in a way unrivaled for low cost, an especially efficient calorimeter and a water jacket excellently adapted for effective stirring. Stirrers and covers only remain to be provided.

Some Limitations. Restrictions are imposed by the shape and brittleness of the vessel. There may be difficulty in inserting structures thru the narrow neck, and certainly in providing evaporation-tight covers for both calorimeter and jacket. A cover across the mouth of the bottle is easy to install, but a second one, either below this or around it, and 1 or 2 cm. from it, is much less convenient. With the adiabatic method, where freedom of evaporation into a small space is often not objectionable, the Dewar with a single cover at jacket tem-

perature even has advantages, in the smallness of the saturated space and of the water surface. A satisfactory scheme for using two tight covers is to be desired, but has not appeared in the 30 years since the calorimeter was invented. A tight cover above, and a nearly tight one below, either floating or with vanes dipping into the water, will do fairly well if the adsorption error with them proves to be small enough. Rubber stoppers, or the total omission of covers, and the failure to make the jacket temperature surround the vessel above as well as at the sides, are generally for crude work.

Metal in Glass

If a complete metal calorimeter is set in a glass jar the small thermal leakage is partly retained, while the disadvantages of the glass tend to be avoided, except the relatively narrow mouth, and the lag, which may become worse, extending to the whole inner wall of glass. A mercury filling, which may be used to overcome the lag, seems dangerous for any but very small vessels, on account of the continual pressure. Water [8] seems to be thermally the next best thing for making contact. Calculation indicates that a glass wall 1.5 mm. thick outside 2 mm. of water would lag about 25 seconds behind the metal wall, and would be within 1 per cent of equilibrium in 2 minutes. For oil the times are 87 seconds and 7 minutes. These are very large lags, but they are multiplied by the very small K of the glass vessel. They are therefore equivalent to lags of about 8 seconds or 28 seconds in an ordinary calorimeter. They would usually be satisfactorily constant, hence not likely to cause appreciable error. Calcium chloride in the water will prevent evaporation, but strict attention will be needed to keep the heat-capacity, that is the quantity of the water, constant.

Advantages in Cruder Work

The sources of error and the inconveniences which characterize the vacuum-walled calorimeter are clearly serious only in work of high precision. Hence its most unqualified success has been in work of low precision. Experimenters who had found temperature loss almost negligible could now disregard it entirely. In more exacting work fewer or cruder measurements could be used. Such savings are of labor, rather than error. This calorimeter helps the experimenter to get more easily the precision which he could have got without it. This precision is easily exaggerated. If the leakage modulus of the vessel is 0.0007, the temperature loss is of the order of 7 per mille for 10 min-

[8] White, Walter P., *J. Am. Chem. Soc.*, **40**, 1871 (1918).

utes, negligible only in decidedly crude work. But if only the difference between φ_x and φ_r is neglected (see pages 42, 124) the error at most is only about 1 per mille, and similarly the precision of most *rapid* methods is increased.

Advantages in Precise Work

Altho most popular now in crude work, the vacuum-walled calorimeter offers aids to precision such as are more imperatively needed for difficult tasks. Nearly all the principal errors are diminished. The error from faulty equalization is diminished; that from convection is practically excluded; the space open to evaporation and the surface adsorption are diminished, the need of following the temperature rise is less urgent. In the adiabatic method, where the chance of error in φ is not remote, the precision and frequency required for its adjustment are diminished several-fold. All these gains, however, are little greater (for the most part by less than a factor of 2) than can be obtained by a convection shield, by using the Adiabatic Method to avoid convection, or by other schemes.[9] Hence the Dewar vessel in precise calorimetry is useful but generally has no preponderant advantage.

Absolute vs. Proportional Precision. Since the variation of heat capacity with height of water sometimes barely escapes being an important source of error, the vacuum-walled calorimeter may be more satisfactory for very delicate measurements than for those of high relative precision.

Having the liquid level low in the flask increases the lag and the uncertainty of the heat capacity, but diminishes the thermal leakiness; hence it tends to be advantageous where delicacy of measurement is the chief desideratum.

Section 23. Aneroid or Unstirred Calorimeters

The calorimeters which Dickinson has christened "aneroid" (fluidless) are really distinguished by absence of *stirring,* since they have proved specially effective for some difficult researches on fluids. Their characteristic feature is that conduction in a solid, commonly copper, is relied on to produce the temperature equalization which is usually furnished by the stirring of a liquid. They have been of two kinds; in one, receiving aneroids, the heat is introduced in a small cavity in a relatively massive block of copper; in the other, synthermal aneroids, the more usual kind, better distributed heat is applied to calorimeter and contents, either electrically, or by thermal leakage to the entire

[9] As has virtually been said by Barry: *J. Am. Chem. Soc.*, **44**, 931 (1922).

surface. When the heat supply is by thermal leakage it may be negative in sign; that is, the actual process may be a cooling. Dulong and Petit's method (1820) seems to be the earliest instance of this kind. Most calorimetric work done entirely at high temperatures has been done by causing a temperature change thru thermal leakage.

Advantages

The advantages of the aneroid calorimeter are: Freedom from stirring and evaporation, and the ability to reach extreme temperatures where the use of liquids is difficult. The method of distributed heating lends itself to rapid determinations of specific heats, one interval following another, sometimes for hundreds of degrees. Yet another advantage in some cases is that the absence of stirring and of fluid circulation renders small dimensions easy to get.

Essentials of Technique

The aneroid calorimeter has one disadvantage, the relative imperfectness of temperature equalization by conduction alone. The special technique of the method consists largely of the means taken to deal with this disadvantage.

The principal means which may be taken are the following:

1. Metal of high conductivity, copper or silver, is used.
2. The heat is generated uniformly, in order that conduction may have as little equalizing as possible to do.
3. The thermal head is kept very small, in order that thermal leakage may not create temperature differences.
4. The measurements to determine the thermal head are made at several points on the calorimeter surface, and the effect of such temperature irregularities as there are is thus diminished.
5. An air space is made to separate the calorimeter wall from the inside, so that heat, coming thru slowly to the wall, will spread over it more uniformly. Since increase of time makes some errors worse, this scheme is of doubtful value, except where some other factor would delay the experiment in any case.

Dimensions in Synthermal Aneroid Calorimeters

From the fundamental equation for heat flow it follows that the time required to get any given degree of equalization varies as the square of the linear dimension. The thermal leakage modulus, proportional to surface and inversely to mass, varies inversely as the first power of the linear dimension. Hence if a calorimeter is diminished

so that its length becomes $\frac{1}{n}$ of the former value, the time of an experiment may become $\frac{1}{n^2}$, the leakage modulus, K, n times what is was, the total thermal leakage $\frac{1}{n^2} \times n$, or $\frac{1}{n}$ as much as before.

The gain comes solely thru the shortening of time. It fails as soon as the time or the dimensions begin to be inconveniently small.

The shortening of time that comes with small dimensions will usually be an advantage in itself, aside from its effect on precision.

Dimensions of Synthermal Aneroids at Low Temperatures. The assumptions underlying the preceding demonstration fail at very low temperatures. At low temperatures the main heat loss is likely to be by conduction along wires, and its relative value increases as the cube, not the first power, of the ratio in which the linear dimension is made smaller. Hence the temperature loss with a small calorimeter is greater, in spite of the shortened time. Moreover, the fall of specific heats to low values at low temperatures increases heat diffusivity. Equalization is quickened as it would be if conduction were increased ten or twenty fold at ordinary temperatures. Rapid rates do well without small dimensions. Hence very small calorimeters, whose construction is also more exacting, are not desirable.

Dimensions at High Temperatures. The preceding demonstration assumed a given error in the internal temperature distribution. The balance of error between this and that from the external flow of heat can be adjusted by changing either the rate or the linear dimension, or both in the *same* direction. An increase of either rate or diameter increases the internal gradient, but lessens either the time or the thermal leakiness. Now in electric furnaces the wall temperature is usually far more uncertain than it is at ordinary temperatures, and the external thermal heat transfer more active; hence it is desirable to manipulate rate or diameter so as to diminish the external error at the expense of the inner. But the rate is usually limited, hence the diameter should be greater than is best at lower temperatures. Since for a given rate the external error varies as the first power of the diameter, the internal as its square, a principle already presented (page 66) dictates that the internal error should be twice the external. But it is hard to know when this ideal is realized in the actual furnace.

On the other hand, however, the furnace should evidently go at its maximum rate unless this increases the lack of uniformity considerably. Usually in furnace aneroid calorimetry the heating is by "radiation,"

i.e., all kinds of heat flow from the furnace cavity wall. Then the smaller the heated body is, the nearer to the furnace in temperature will it be, for a given rate. A small body, therefore, can, with the most advantageous rate, that is, the fastest, be carried nearer to the highest temperature the furnace will stand. This is often a prevailing argument for small size.

Synthermal Aneroid Calorimeters at High Temperature

Furnace aneroids have usually been calorimeters more in performance than in appearance. A platinum capsule of thimble size, with a single couple imbedded in the material it contains, is often all there is to it. The difference of temperature between the junction and the platinum surface is small and regular enough to be satisfactory.

The Twin Method in the Furnace. The twin method, usually called in this connection the comparison body or "dead body" method, is very advantageous. It does not in furnaces particularly improve the temperature precision, but it lessens very greatly the uncertainty in estimating the effect of the furnace, an uncertainty arising from lack of vertical uniformity, from fluctuations in temperature, and from lack of knowledge as to the coefficient of heat transmission or lag.[10]

The quantitative determination of heat is still not secured by this means alone. It has been estimated [11] that a latent heat of transformation as small as 0.1 calory per gram per minute can be *detected* by the wabble it produces in the differential temperature curve as high as 1500°. But the change in heat flow corresponding to a larger difference of temperature cannot be *estimated,* because it cannot be told what part the difference is of the total difference between furnace wall and calorimeter, and also because the coefficient of flow from one calorimeter to the other is unknown. A calibration, however, should make it possible to evaluate the difference curve, and more easily than for a single calorimeter, where an attempt to determine the effective furnace wall temperature would be a more important part of the task. A new and interesting field seems offered here, and one likely to be useful for important substances melting from [12] 800° to 1200°. The twin aneroid just referred to is shown in Figure 14. The supporting tubes are objectionable here in being too heavy. Up to 1500° temperatures could be read with fair certainty to 0.05°. Over the whole interval from

[10] It *might* be worth while, and usually would not be difficult, to give the pair of calorimeters an oscillating rotation about a vertical axis, and thus eliminate the effect of horizontal temperature inhomogeneities in the furnace.

[11] White, Walter P., *Phys. Rev.,* 32, 604 (1911).

[12] At lower temperatures, Dr. A. B. Lamb informs me, experiments are in progress with stirred twin calorimeters in furnaces.

1200° to 1500° and with a rate of 10° per minute results could be repeated to about 0.1°. One-tenth of a degree corresponds, in the case tested, where silicate charges were used, to about 0.07 calories per

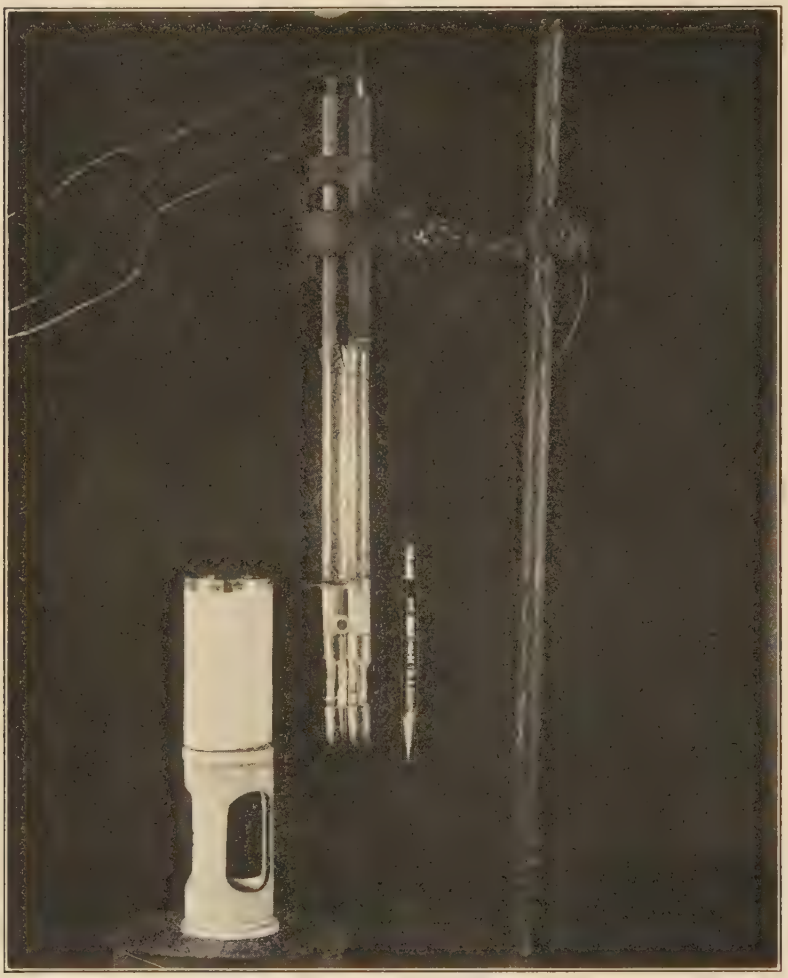

FIG. 14.—Twin aneroid calorimeters of platinum, for use in electric furnaces up to 1500° C., with platinum-lined inclosure to diminish thermal leakage and give a steadier and more uniform surrounding temperature. The pencil is included to show the size.

minute, or 0.03 calories per gram per minute, but this was 1 per cent of the total heat per minute. There was no recharging or shifting.

It was found, near 1200° especially, that if the furnace had been heated within a few hours previously the difference temperature was

altered about 0.4°. This was undoubtedly due to the effect of the ends of the furnace, which warm up tardily, and shows that these affected the calorimeters perceptibly and unsymmetrically, altho the arrangement had been made as symmetrical as seemed possible. This is a good example of the difficulties attending this kind of work.

Other Methods. A serious effort was made to determine latent heats in electric furnaces, using a sheet platinum box, whose temperature was measured, as the calorimeter chamber. But it turned out that the temperature of the middle of this box was too far from that of the ends to admit of results certainly more accurate than 10 per cent.

Other methods, all very simple, of calorimetry in electric furnaces are discussed elsewhere.[13] The implied condemnation there of the twin method on account of the complicated interpretation of its results has just been withdrawn, a few lines above in this section.

In fact, there is strong reason for suspecting that the quest for simplicity has been sadly overdone in this department of calorimetry. In particular, experiments not yet published have shown that electric heating in furnace calorimeters is surprisingly easy and satisfactory, at least up to 1200°. Final quantitative results are not now available, but some gain in precision seems assured, since the electric arrangements leave unimpaired all the effectiveness which the calorimeter had before they were added. As a means of calibration, especially, the electric heating is more conspicuously superior in the furnace than at room temperatures.

The presence of the heater inside a small calorimeter renders it undesirable to have the thermel there also, and calls for a measurement of the surface or wall temperature. But this is a gain, anyway, rather desirable even in the absence of electric heating. For of the two thermal quantities, temperature and heat-quantity, the determination of heat-quantity now presents the greatest difficulties. This is determined by means of the surface temperature, which therefore needs chief attention. Moreover, in measuring wall temperature the calorimeter wall itself can be the thermojunction, being made of the two thermoelectric metals. And in that case the line of contact can run around the calorimeter in an oblique plane, thus integrating the temperatures at different heights and on different sides.

High Temperature Aneroids vs. "Dropping" Method. Where more time can be given to the securing of higher precision, these interesting aneroids seem inferior to the plain old method of tracing the

[13] White, Walter P., *Am. J. Sci.*, **28**, 474 (1909); *Z. anorg. Chem.*, **69**, 345 (1911).

heat quantity curve by dropping into a calorimeter from a furnace at one temperature after another. The main objection to this method is that heat capacities at higher temperatures must be determined as smaller differences between larger quantities. For example, the heat required to raise a substance thru the hundred-degree interval from 1200° to 1300° is the total heat from 25° to 1300° less that from 25° to 1200°, with the errors of the two large results included.

As far as the actual determination of heat goes, however, the error of the two large results in the water calorimeter is decidedly less than that of one small one in the furnace 1000 or more degrees higher. The accidental errors in the two droppings also are at least somewhat less.[14] There remains only the temperature measurement in the furnace. But this affects similarly both kinds of experiment. If there is, for instance, a thermometric error of 1° in measuring the interval from 1000° to 1100°, it is easy to see that the resulting error in the specific heat over that interval is the same for both methods. Any error there may be in measuring up to 1000° cancels. In the dropping method the furnace temperature when measured is constant for a considerable time after coming to equilibrium, and may be read more accurately than the rapidly changing temperatures in the aneroids.

There are, however, 3 points in favor of the aneroids. (1) If the error in reading the furnace temperature varies from one set-up to another, the dropping method will be affected, the aneroid very little. (2) For very short intervals, say 10°, the final proportional error in the heat as measured by the dropping method will be proportionally larger; that of the aneroid probably not so much larger. There is, however, little use in measuring intervals as short as this where the heating is by transfer from the furnace wall. If a change of state occurs, several minutes will be required to restore the equilibrium temperature distribution, and in that time the furnace will have risen at least 30°. But with electric heating in the calorimeter the furnace can be nearly or quite stationary. (3) If oxidizable materials need to be protected from the air, this is done much more easily with the stationary aneroids. An important field of work thus lies especially open to them.

Aneroids at Low Temperatures

Aneroid calorimetry at low temperatures has been much improved within the last seven years, principally by providing an environment which can be kept somewhere near the temperature of the calorimeter, and by stopping the flow of heat from the outer air down lead wires.

[14] A discussion of methods for lessening these I have given in *Am. J. Sci.*, **47**, 54 (1919); and have added another method in *Chem. Met. Eng.*, **25**, 20 (1921).

Aneroids at Ordinary Temperatures

A low temperature synthermal aneroid has been reported as unsatisfactory at ordinary temperatures, but an aneroid designed for them gave very accurate results at the Bureau of Standards, without any vacuum.[15] Its principal feature, as compared to the usual low temperature aneroid, and probably the chief factor in its success, is the measurement of temperature over the surface by means of distributed thermocouples.

Since these couples were put in series electrically to secure sensitiveness of reading they could not be soldered to the metal surfaces, and were imbedded. But since the copper was rather thin, and the boring of long fine holes in copper is extremely difficult, the imbedding was done by putting the wires in copper tubes, which were soldered to the surfaces.

Measurement of Surface Temperature. The measurement of surface temperature in an unstirred body is a characteristic and very important feature of the aneroid. Three errors appear to be possible. (1) Lag of some of the couples. This, like any other lag, produces, if constant, no error in an experimentally calibrated calorimeter. Its final temperature effect is $fLK\Delta\Theta$, where f and L are lag constants (Equation L2, b; page 88); K, the leakage modulus; $\Delta\Theta$, the temperature rise. The effect is independent of the time of the experiment, or the form of the temperature rise curve. (2) Some junctions may be influenced by the jacket temperature. This is equivalent to a slight change of sensitiveness in reading the thermal head, and causes no error if constant. (3) The average reading of the junctions may not be the same as the average temperature of calorimeter or jacket surface. For instance, if 2 junctions are used, and a small portion of the surface is hotter than the rest, then if this portion is not very near either junction its excess temperature will not be taken account of; if one junction happens to be on it, the reading will evidently be too high.

Four things lessen this error.

(a) Increasing the number of junctions

(b) Distributing them evenly

(c) Having the surface temperature uniform

(d) Having the pattern of surface temperature constant, since all the temperature differences in the calorimeter, including those between junction and metal, will then always be in the same proportion; the error will be proportional to the rise, and thus equivalent to a slight

[15] Dickinson, H. C., and Osborne, N. S., *U. S. Bur. Standards Bull.*, **12**, 23 (1915); **14**, 133 (1917).

change in the sensitiveness of the thermels measuring that. Reproducibility of surface temperature distribution, therefore, is to be classed with uniformity, and sufficiency in the number of junctions, as one of three things either of which, in perfection, eliminates error, while the errors of each are made harmless if the others are present in a fairly high degree. Quantitative data, sufficient to guide construction, regarding these three sources of error are wanting. Reproducibility of temperature distribution calls for fixedness of parts as far as is possible, and for broad, well fitted surfaces, carefully freed from powder or dust, where metals come together without soldering.

Receiving Aneroids

In the synthermal aneroids, just described, specific or latent heat is measured by supplying heat to the body and to the calorimeter which is heated with it. It is therefore a merit for the heat capacity of the calorimeter to be small. The "calorimeter" contains, protects, equalizes heat, and actually disappears when the body experimented on is a metal, able to perform these services for itself, as in Gaede's pioneer work and that of the Griffiths.

In the other type, receiving aneroids, heat is given to the calorimeter and measured by its change, and the calorimeter is usually rather bulky, and, if of copper, more than rather heavy.

Advantages. Its advantages, compared to the water-filled calorimeters doing similar work, are absence of evaporation, freedom from stirring arrangements, and escape from the labor of removing, filling, weighing, and replacing for each experiment. In dropping from a furnace the avoiding of the splash and the steam production deals with their errors more simply than do other procedures. A more decided advantage may come in handling objects that can not be exposed to water, for failure has usually been reported for metallic inclosures which were to be dropped from furnaces into water and remain tight.

Disadvantages. The only noteworthy disadvantage appears also to come in dropping bodies into the calorimeter, and to be the difficulty of getting the heat to the copper. For reasonably quick transfer the capsule or tube that holds the material tested should fit fairly well the hole in the copper block, hence a special container must be provided. But the shock of dropping such a structure, thin-walled as it must be, into a rigid cavity, seems bound to necessitate frequent repair or remaking, and this is decidedly expensive if the material is platinum. For furnace temperatures where gold or silver can be used the problem is easier.

The only alternative seems to be silica glass, dropped into water, and this will not go many times to temperatures much higher than can be reached with gold, while its heat capacity is much larger than that of a metal container. So for hydrophobic experimental material the receiving aneroid and the metal container seem the best thing there is. For excluding oxygen the silica glass container with all its disadvantages seems the best thing there is.

Different Uses. The receiving aneroid can also be used for thermochemical work, but this is ordinarily not a natural use for it, since one of the advantages of this calorimeter is freedom from the need of stirring.

It seems almost ideal for combustions, with the bomb and copper block perhaps combined or identical. Féry [16] has proposed a very crude form for this purpose. The necessity of using the adiabatic method for really good results is against the commercial use of better forms, but the saving of labor and of one of the worst sources of error, evaporation, is a strong argument in favor of the aneroid. The more familiar resistance thermometer, tho not as appropriate as the thermel, would be good enough for most work, and there is nothing to prohibit the thermel. Of course a distributed, integrating resistance thermometer is in mind here.[17]

The Geophysical Laboratory Aneroid

The receiving aneroids thus far described have been decidedly crude, which is not necessarily a reproach in view of the frequent limitations of the auxiliary determination in the furnace. More refined calorimeters have been proposed, but as far as I know not yet described. Such a one is in use at the Geophysical Laboratory, intended for work with a furnace of specially uniform temperature. It is shown in Figure 15. Its chief features are (*a*) the thermels, (*b*) the method of closing, and (c) the arrangements for removing the container.

Its Thermels. The thermels, of constantan wire 0.25 mm. in diameter (No. 30) and copper 0.08 mm. (No. 40), are set in grooves along the sides of the copper block. They can thus be given a better fit, and consequently less lag, than in a tube, and yet can be taken out much more easily. Rosin-and-beeswax was first put in the grooves, the block was kept by its own heater at a temperature just short of the softening region of the wax, and the wires were pressed in with a piece of hot sheet copper. Bare wires or thin pieces of wood were then

[16] Fery, C., *Compt. rend.*, **154**, 691 (1912).

[17] *See e.g.* Dickinson, H. C., and Osborne, N. S., *U. S. Bur. Standards Bull.*, **12**, 33-37 (1915).

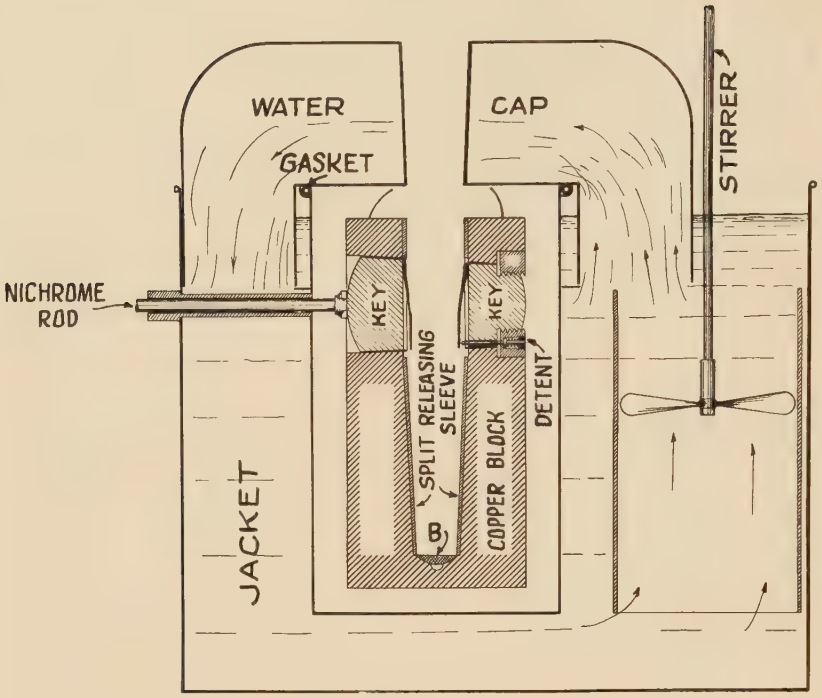

Fig. 15*a*.

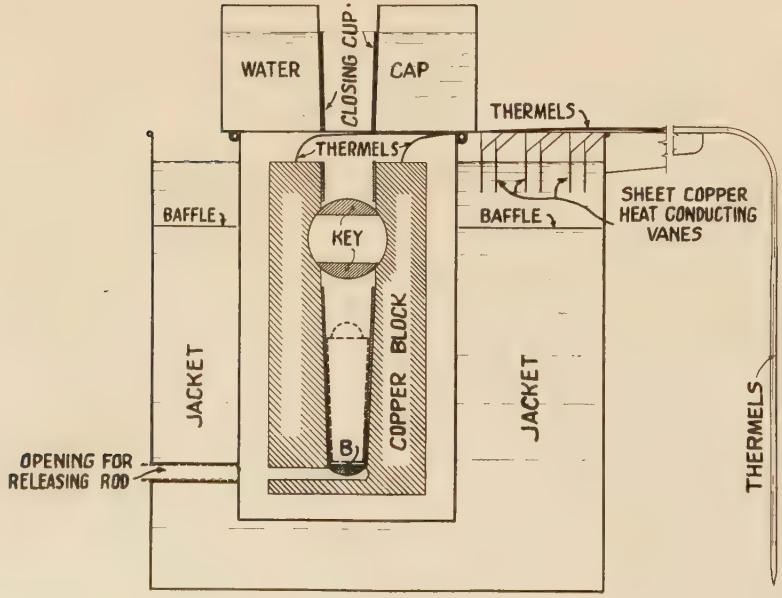

Fig. 15*b*.

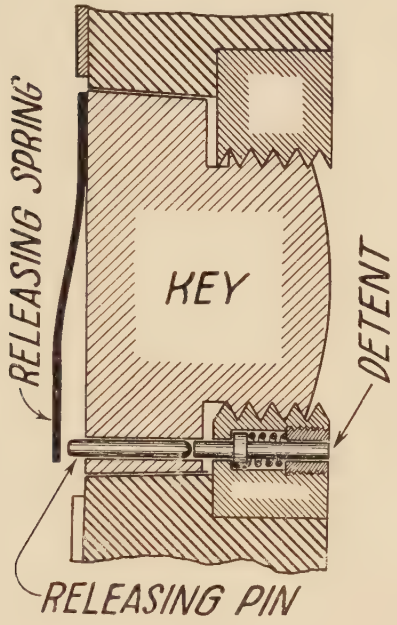

FIG. 15*c*.

FIG. 15.—Copper-block "receiving" aneroid calorimeter, closed by the automatic turning of a brass stopcock key. The jacket has a thermostat and rapid electric heating. B is the releasing button, which in case of necessity can be used to pry up the releasing sleeve to free the object which has been dropped in. 15*a*, open. 15*b*, closed. 15*c*, detail of detent release for the automatic closing. The falling container presses the releasing spring against the releasing pin, and that against the detent. The block is 7.8 × 16.8 cm.

crowded into the groove to insure that the thermel remained in place at all temperatures, and also, where metal was used, to shut out the effect of external temperature. (Heat-insulating material is little better for this than the wax or the air.) Since even metal thus forced in is likely to lag behind the block itself, such wires should preferably not touch the thermels. But the lag is less objectionable than exposure to the outer temperature. The thermel wires were silk-insulated, shellacked. The junctions, which were soft-soldered parallel, and not twisted, were reinsulated by laying under them thin pieces of mica, which folded around them as they were pressed into the grooves.

A great deal of time was lost by the breaking of the fine copper wires, and the taking out of one for repair often led to the breaking of others. The trouble was very largely overcome by making the grooves deep enough to avoid everything like crowding, by keeping the

copper wires a little slack as the others were pushed in, and by the mechanical fastening, which greatly lessened the amount of disturbance after the wires were once in place.

Depth of Grooves, Lags. Altho when this calorimeter is cooling with a perceptible thermal head the ends are an appreciable fraction of a minute ahead of the middle, calculation shows that the radial lag per centimeter next the cylindrical surface is a little less than 2 seconds. Hence the grooves may without hesitation be made several millimeters deep.

These differences of external origin are insignificant compared to those produced by hot bodies inside the calorimeter, and hence are negligible. Nevertheless, to avoid convection an approximation to adiabatic control will be used. The final rise-and-rate readings are to be made with zero thermal head.

A difference of temperature between the extreme ends of the block falls to half value in 30 seconds, or beyond utter negligibility in 6½ minutes. If a few minutes are required to get the heat out of the experimental material, it is clear that the difference in speed between this calorimeter and a stirred one is trifling.

The Method of Closing. As soon as the hot body is in the calorimeter it seemed necessary that (1) Two partitions, (2) each separately in excellent thermal contact with the main block, should (3) instantly close the opening above. In accordance with a suggestion of Mr. H. S. Roberts, all this was accomplished by an automatic stopcock. The key of this stopcock, when turned shut, presents two horizontal partitions across the hole, and is partly split so that the direct thermal contact between them is rather small. The key ends in a screw, and, in turning, becomes tight only at the end of its rotation. It is rotated by a weight, easily accessible outside the jacket, which communicates by a rod turning in a tube running thru the jacket water to the calorimeter chamber. This rod is of poorly-conducting metal (Nichrome), but can be pulled away from the calorimeter as soon as the turn is made, so as not to conduct heat from it. The detent holding the key from turning is released by the passage of the hot body thru the open stopcock, as shown in Figure 15c.[18]

Releasing the Container. The calorimeter, once installed, does not have to be moved from its place in its chamber. But the container, tho after cooling it usually is not tight, might be so, and the removal of the calorimeter to release it would be quite a chore. Hence a releasing

[18] This contrivance was designed by Mr. C. M. Shaw, the Master Mechanic of the Laboratory.

arrangement is provided in case of emergency. It is a split sleeve of copper, 3 mm. thick, which is slightly sprung together as it is pressed down into the conical hole in the block, which it fits with good thermal contact. The container comes to rest in this sleeve. If the container sticks, the sleeve can be pushed upward. It then comes where the diameter of the hole is slightly larger, it springs out toward its normal diameter, and everything is loose. The sleeve can be pushed up by a rod, thrust in from a tube running thru the jacket opposite to a lateral hole in the calorimeter near the bottom.

Section 24. Convection Shields

For many years shields of sheet metal have been used between calorimeter and jacket wall to diminish thermal leakage. Some European writers still speak of them as a customary feature, while they have been little used in this country. Dickinson has rather condemned them on account of the lag of their temperature. A mathematical treatment of such intermediate shields has been repeated in the section on Lag (page 95). Rightly employed, they seem to have considerable value, but the exact source of this value, and the best way to realize it most fully, have not been generally known.

Effects of the Convection Shield

The effect of convection shields on heat transfer by radiation is to diminish it by dividing the total temperature gradient among two (or more) spaces, so that the temperature difference between each pair of surfaces is less; the rate of diminution which holds for radiation also holds for gaseous conduction at pressures so low that the mean free path becomes greater than the thickness of the gaps. Such shields have no tendency whatever to diminish conduction in ordinary air. Since radiation should be, and usually is, a minor factor in ordinary calorimetry (in spite of the frequent unfortunate use of "radiation" where thermal leakage is meant), the diminution of it by a metal shield is of little importance. The real advantage of the shield comes indirectly, thru its effect in decreasing convection. In an air gap of 0.5 cm. there is seldom appreciable convection, so a shield in it is nearly useless. With a shield in a 2-centimeter gap there are, in effect, two 1-centimeter gaps in series; with little over half the conductance of one. The increase in distance is the direct cause of the gain, but the increase would usually not be desirable if in one wide gap, on account of convection. By practically preventing convection the shield makes the gain realizable.[19]

[19] Dickinson's discussion of the value of the shield, which antedates his own valuable work on convection, is misleading. It is based on the hypothesis: "If it (the leakage modulus) is

For very small temperature differences, where convection is slight, the same thickening of the total gap can be obtained without a shield as ordinarily with it. This has been touched upon under the adiabatic method.[20]

Table IV shows that doubling the air gap does less than halve the conduction, on account of the increasing width of the leakage paths. The value of successive increases in the total gap thickness diminishes very rapidly for another reason, also. Consider, for example, a case where the lines of heat flow are parallel. A doubling of the gap thickness would then reduce the thermal leakage to one-half. To cut this reduced leakage in half again would require a doubling of the already doubled gap; the leakage could then become a quarter of the original. Hence the diminution in leakage, a quarter of the original, would be only half as much as was secured by the first and smaller change. A second shield, therefore, is much less useful than the first, and will seldom be worth while.

Closure of the Shield. Since the function of the convection shield is to prevent circulation of air it must be closed fairly tight at one end, preferably at the bottom. The shield thus may take the form of an ordinary can, with a horizontal bottom. Since no shield is needed below a calorimeter that is never colder than the jacket, with such calorimeters —that is, with the great majority—the shield may, if that is more convenient, have no bottom, but be extended below down to the floor of the calorimeter chamber. The extension should of course be by poorly-conducting material, so that it seems generally easier to have a bottom which is part of the shield. Horizontal shielding above the calorimeter is important. It is very inconvenient to make this part of the shield at all tight, but that is not necessary if the bottom is so.

Advantage of a Diminished Thermal Head

Since the shield distributes the temperature gradient over two gaps it not only prevents convection from increasing, but, on account of the smaller temperature difference in each space, will make it very much less than with a single gap as thick as either of the two which are separated by the shield. With the gradient across each gap half of the

nearly independent of distance," and leads to the conclusion that with "a sheet halfway between extended parallel surfaces of the calorimeter and the jacket and not too near either" the loss of heat will be "half of what it would be if the sheet were not there." But the hypothesis is true only when an increase in gap thickness increases convection just enough to compensate for the loss of air conduction, that is, only for gaps of certain thicknesses, and at a different thermal head for each, and when convection is already enormous, relatively. Hence the conclusion is false, as a rule; the most important function of the shield, preventing convection, is not suggested.

Dickinson's very different value for the heat capacity of the shield is explained on pages 95 and 96 of Section 10.

[20] Compare Barry, *J. Am. Chem. Soc.*, **44**, 920 (1922).

temperature rise, the convection, by Table III, will be diminished to about $\left(\frac{1}{2}\right)^3$ or one-eighth, and since convection is proportional also to the cube of gap thickness the gap may be $\sqrt[3]{8}$ or 2 times as thick. And this is true of each gap. One shield, therefore, enables the total gap to be 4 times as thick as without it, for the same convection.

Effect of Shield Lag. Unfortunately, the full advantage of this fourfold gap usually cannot be realized, on account of the lag of the shield. Only after a comparatively stationary temperature has been reached is the thermal head between calorimeter and shield half of the whole. During the temperature rise the shield lag causes this thermal head to have more than its final value in the inner gap, with considerably more convection. There is a compensation, however. The ordinary convection error is due to the fact that convection, being proportional to the cube of the thermal head, is disproportionately low at the intermediate temperature. Since this tendency is opposite to that resulting from lag, the two tend to neutralize each other.

The error remaining was calculated for several cases, and the results are shown in Table VII. The method used is as follows: It is a sufficient approximation, in determining orders of magnitude, to take the convection effect as proportional to the cube of the thermal head. Hence the calculations deal only with this cube. The convection, that is, this cube of the thermal head, φ, in the inner gap, between calorimeter and shield, was the one treated. As in Section 8 the approximate calculation is simplified by taking the temperature rise as linear in a short time, T_B (Fig. 8), and by taking $\varphi_0 = 0$. In actual work the convection effect is measured in the rating period along with the other thermal leakage, and the corresponding effect in the X-period is computed, in accordance with any of the equations (6) to (13), as if it were simply proportional to φ, that is, it is multiplied by φ_x/φ_r. Taking φ^3 as representing the convection, $\varphi_r{}^3 \frac{\varphi_x T_B}{\varphi_r}$ stands for the convection effect as computed. Since the rise of the calorimeter is taken as linear, the average φ_x for the time T_B is $\varphi_r/2$ with sufficient accuracy for the present purpose; hence the convection effect during T_B, as computed in an actual determination, corresponds here to $T_B(\varphi_r)^3/2$. The error, where no shield is used, is the difference between this quantity and $\int_{T_B} \varphi^3 dt$, which corresponds to the true convection effect; this error is easily shown to be $T_B(\varphi_r)^3/4$. (Compare Equation 26.) With the shield there must also be added the excess convection just after the

end of the time T_B, while the shield is coming to its equilibrium temperature.[21] This is the largest part of the error for small values of T_B.

The total gap thickness was taken as 2.4 cm., which makes the lag of a silver shield 0.05 mm. thick 0.5 min. The gap thickness without the shield was 1.2 mm.; the same as either half gap with it. The difference in the final convection, therefore, was due to the diminished thermal head across each gap with the shield. Since this was one-half as great as without the shield, the *rating period* convection was one-eighth as much. The temperature rise, $\Delta\Theta$, was taken as 5°, but any other would have given the same ratios between the different quantities, tho different absolute magnitudes.

TABLE VII.—Convection Error Due to Lag of a Convection Shield.

	Shield Lag L	Time of rapid rise T_B min.	Total $\varphi^3 T_B$, proportional to convection				Error, equal to difference of actual and computed	
			Actual		As computed by temperature lag formulas			
			With shield	Without shield	With shield	Without shield	With shield	Without shield
1	0.5	8	**41**	250	**62**	500	**—21**	—250
2	0.5	4	**28**	125	**31**	250	**—3**	—125
3	0.5	2	**24**	62	**16**	125	**8**	—62
4	0.5	1	**26**	31	**8**	62	**18**	—31
5	0.5	0.5	**30**	16	**4**	31	**26**	—16
6	0.5	0	**38**	0	**0**	0	**38**	0
7	1	8	**56**	250	**62**	500	**—6**	—250
8	1	4	**48**	125	**31**	250	**17**	—125
9	1	2	**52**	62	**16**	125	**36**	—62
10	1	1	**59**	31	**8**	62	**51**	—31
11	1	0.5	**85**	16	**4**	31	**81**	—16
12	1	0	**75**	0	**0**	0	**75**	0
13	φ^3 in rating period		15.6	125				

The most striking thing shown by the table is the detrimental effect of even a moderate increase in the lag of the shield. (Lines 10-12.)

[21] The calculation was made by finding the lag of the shield as in the paragraph headed "Lag," two pages further on. Equation 43, just below, was then applied to find the shield temperature, and hence φ. $A/2$ and $V/2$ were taken as determining the temperatures toward which the shield was coming. By well-known methods $\int\varphi^3$ was then found, first for the time T_B, and then for an infinite time thereafter, which was practically only a very few minutes. The calculations were much shortened by getting two formulas, in which the different numerical values could be substituted.

Equation 43, referred to above, is (2), in *Physical Review*, 31, 562 (1910). It gives the temperature of a lagging body following a body changing at a constant rate. If the temperature of the leading body is $A + Vt$, and L is the lag, we have the temperature

$$\theta = A + Vt - LV + (\theta_0 - A + LV) \cdot e^{-\frac{t}{L}} \qquad (43).$$

A lag of 1 minute is that of a silver shield only 0.1 mm. thick, or of one 0.05 mm. thick in a gap 4×1.2 cm. thick.

In so far as this result demands very thin shields it only falls in with several other peculiarities of the convection shield. Moreover, while a thickness of only 0.05 mm. may be near the limit, we have found it mechanically quite satisfactory. Hence the addition of one more reason against shields much thicker is not a matter for regret.

It also appears, however, that the larger lag resulting from a gap of 4 cm. or so, even with a silver shield only 0.05 mm. thick, will often rule out such gaps, tho the lag due to the very wide gap is actually an advantage with slow temperature rises.

This prohibition of gaps 4 cm. and over is of negligible importance as far as the attainment of small values of K is concerned, since, as Table IV shows, the rate of gain has become trifling by the time 3 cm. is reached.

As to the convection itself, in a calorimeter adapted to more than a limited range of conditions the shield evidently will sometimes do no more than hold the convection error about where it is while securing the small value of K, the leakage modulus, which comes from a doubled gap. Thus the thinner shield in the case for it most unfavorable, namely, an instantaneous rise, gives a convection error of about the same amount as occurs without it in a very frequent case, that is, a rise occupying about a minute. But usually it will do better than this, while it gives a remarkably small error in the very cases where without it convection error would usually be so large that a recourse to the adiabatic method would be imperative—that is, in the slower rises.

In Table VII the values for convection with the shield apply to a twofold total gap. If the convection without the shield were calculated for this gap the error for $t = 0.5$ minute would be -125, the rating period convection, about 64 times as much. Among the errors diminished by the small K that comes with the wide gap are those from lag, including the effect of insufficient stirring, from jacket temperature change or uncertainty, and that in following a rapid temperature rise.

None of the errors with the shield given in the table is serious in actual magnitude. It is shown in Section 8 that the error without the shield for 2 min., 5°, and 12 mm., here given as 62, is $\frac{2}{4} K\Delta\Theta, = 0.000\,033\Delta\Theta$, and therefore is negligible for 0.3 per mille precision, about the highest yet reported in calorimetry. Hence the very worst error with a shield in Table VII is practically negligible. For 0.1 per

mille precision a diminution of the gap, say to 2 cm., might be desirable with a convection shield.

Design of Shield

If the shield is to be free from disadvantages it must be properly designed. (1) Its lag must be small, and (2) its effective heat capacity constant.

Lag. *The lag,* by section 10, is $\frac{1}{K_1 + K_2}$; for a shield midway between outer and inner surfaces $K_1 = K_2$, approximately, and each is equal to the rate of heat loss divided by the true heat capacity. For a silver shield 0.05 mm. thick the capacity is 0.003 cal. per degree per sq. cm. nearly, since the volume specific heat of silver is 0.578. The rate of heat transfer per cm. cube of air is 0.00006 cal. per sec., or 0.0036 per minute by conduction, to which radiation adds a little. Hence $K_1 + K_2, = 2K_1$, comes to over 2.5 per minute for 1 cm. gap, or the lag is 0.4 minute. For a calorimeter of 1 liter the heat capacity of the shield 0.05 mm. thick will be of the order of 2 per mille; its effective capacity, by **(L15)** page 95, 0.5 per mille. The effect of shield lag can be sufficiently seen by considering the simplest case, that where the temperature rise in the calorimeter is instantaneous. The shield then approaches exponentially its final temperature $\frac{C + \Theta}{2}$, where C is, as before, the jacket temperature. Taking this as zero, and Θ_o also as zero, ADG in Figure 16 represents the shield temperatures.

The ordinary temperature loss calculation treats the X-period shield temperature as equal to its rating period value, $MN = AB = \frac{C + \Theta}{2}$. The deficiency from this value, the shaded area in the figure, is the total or integrated shield lag. The lag effect is this area multiplied by the thermal leakiness of the calorimeter to the shield, K_3, and is readily found as follows: By **(43)** the equation of the curve ADM is $\frac{\Delta\Theta}{2} e^{-2K_1 t}$. Hence, by **(18)**, its area is $\frac{\Delta\Theta}{2} \times \frac{1}{2K_1}$, and the lag effect is $\frac{\Delta\Theta}{2} \frac{K_3}{2K_1}, = \frac{\Delta\Theta h}{4H}$, where h and H are the respective heat capacities of shield and calorimeter. The corresponding effect for the shield itself is $\frac{\Delta\Theta}{2} \frac{2K_1}{2K_2} = \frac{\Delta\Theta}{2}$, which means twice as much *heat* as does $\frac{\Delta\Theta}{4} \frac{h}{H}$ in the calorimeter. More heat accumulates in the shield than the extra loss from the calorimeter in heating the shield, because the lower

temperature of the shield along AD causes it to lose less heat at the same time that it gains more. (Equation **15** has thus been demonstrated for the special conditions assumed, and the demonstration could easily be made more general.) The lag effect, as already explained (Section 10), is proportional to $\Delta\Theta$ for unchanging shield as long as the jacket temperatures are constant, and is taken care of in the calibration. If,

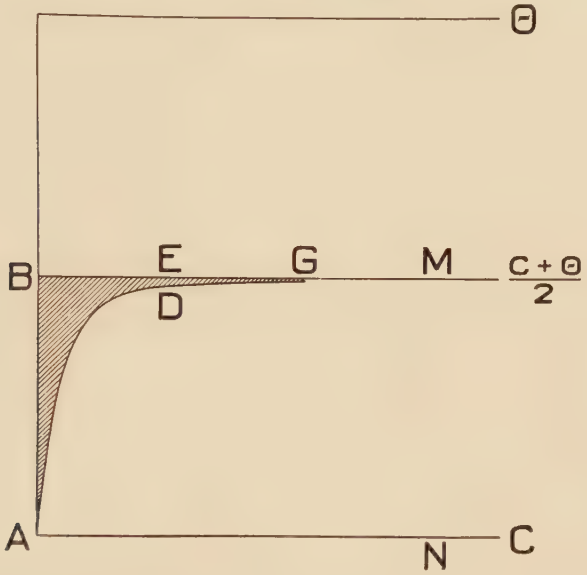

FIG. 16.—Diagram illustrating the lag of a convection shield for instantaneous calorimeter temperature rise. ADG, shield temperature.

however, the rating period is begun before the exponential term of (**43**) has become negligible, that is, before the curve at D has come to differ from its asymptote by a negligible amount, as at G, the special heat loss DGE will not have occurred in the X-period, and it will be included in the rating period, causing the calculated temperature loss to be too high. For equal length periods the error will thus evidently be twice DGE. Hence it is $2DGE$ which must be made negligible. But DE, by (**43**) is $\frac{\Delta\Theta}{2}e^{-2K_1T}$, and hence by (**18**) $DGE = \frac{\Delta\Theta}{2} \times \frac{1}{2K_1}e^{-2K_1T}$ and the corresponding heat quantity is $\frac{\Delta\Theta}{4}\frac{h}{H}e^{-2K_1T}$ or $2DGE = \frac{\Delta\Theta}{2}\frac{h}{H}e^{-2K_1T}$. For 0.1 per mille precision, therefore, or an error less than 0.000 01, $e^{-2.5T}$ must be less than 0.01. From a table of exponentials it follows that T may be as short a time as 2 minutes, or 1 minute for 1 per

mille precision. The necessary time evidently increases as the thickness of the shield. If the rise is not instantaneous T is the time after the main part of it.

If the jacket temperature varies so does the lag effect (Equation **L14,** page 95). Herein may lie a stronger reason for very thin shields than that based on Figure 16.

Constancy of Effective Heat Capacity—Change of Position. The effective heat capacity of a convection shield may be changed from two causes, (1) shift of position, (2) change in emissivity. If we assume that $K_1 \propto \frac{1}{s}$, $K_2 \propto \frac{1}{S-s}$, where S is the total gap thickness, s the inner gap, and if L is lag, it is easy to show from (**L15**) that:

$$dL = -\frac{2h}{H}\frac{K_1K_2}{(K_1+K_2)^2}\frac{ds}{s} \qquad \textbf{(44)}\ ^{22}$$

If we make the crude but sufficient assumption that $S = 2s$ and $K_1 = K_2$, then $dL = -\frac{h}{2H}\frac{ds}{s}$. A total shift of the shield thru 1 mm. with two 1-cm. gaps changes the effective capacity by $\frac{h}{20H}$, or by 1/5 its normal value; or about 0.1 per mille ordinarily, for a silver shield 0.05 mm. thick. A change of 1 mm. for one-tenth of the shield would therefore give, for a liter calorimeter, the error of 0.00001 $\Delta\Theta$ which is just barely negligible for 0.1 per mille precision. Since an inward displacement of one part of the shield is usually accompanied by a nearly equivalent outward displacement elsewhere, an error of this magnitude ought to be very rare with a shield 0.05 mm. thick, but the shield had better be given some stiffening or support. The error from such a shift evidently amounts to a change in the calibration factor, or heat capacity, of the calorimeter.

Surface Change. A change in the radiating power of the surfaces bordering the gaps will alter the K's of Formula **L13,** page 94, and will cause error if its effect is different for the two gaps. This will certainly be the case if the calorimeter surface is soiled, as by handling, and may even occur thru irregular tarnishing. We have investigated the effect of some surface changes.[23] One surface was of glass, which comes near being a perfect radiator at ordinary temperatures; the other was of silver. The gap thickness was equivalent to 11 mm. A complete coat of tarnish, produced by dilute ammonium sulfide, added 3 per cent

[22] This equation is more generally true than the one (L 27) given in 1918, tho both give the same result in the present application.

[23] White, Walter P., *J. Am. Chem. Soc.,* **40,** 1898 (1918).

to the previous heat transfer, due to air conduction and radiation. Special effort raised this to 12 per cent. This was opposite the excellently absorbing glass surface; the effect would have been less against a metal surface, even if equally tarnished. The effect of soiling the surface by a film of oil was greater, as was to be expected, but a badly soiled calorimeter facing a tarnished shield, the worst combination likely to occur in practice, will evidently give less than 10 per cent increase in K_1. It is easy to show that for a small increase, ε_K, in one of the K's of **(L15)** the effect is $\frac{1}{4}\,\frac{\varepsilon_K}{K}\,\frac{h}{H}\,\Delta\Theta$, or 0.05 per mille for a 10 per cent increase with a shield 0.05 mm. thick, even with a calorimeter holding only a liter. But an amount of soiling sufficient to approach remotely this result would be disgraceful; the effect of tarnish can evidently be quite negligible.

Thickness. The conditions governing the best thickness of a convection shield are easily stated. A very thin shield is more liable to error from displacement of some part of it, but this disadvantage tends to be counteracted by the smaller heat capacity that goes with thinness. The lag and the error from surface change both diminish as the shield thickness. Hence the shield should be as thin as can be and still avoid error from change of form. This appears to call for shields never over 0.1 mm. thick, while a satisfactory silver shield 0.05 mm. thick has been constructed in our laboratory. Since the matter of thinness has not previously been much emphasized, it seems probable that many existing shields are seriously defective in this respect.

An increase of gap thickness evidently increases the time for equilibrium. The final effect of surface change and the lag effect are unaltered. The effect of a given change of position is diminished. Hence displacements become less important, thinness, more so. The thicker is the gap the smaller will be the most advantageous shield thickness.

The Measured Shield [24]

Measurement by thermels distributed over the effective surfaces is a method of superior precision for determining thermal head. The only reason for not using it widely is that it is ordinarily unnecessary. The inconvenience attending the use of numerous attached wires can be greatly diminished by Dickinson's separable combination.[25] Still more convenient is the arrangement which I suggested in 1918, of running

[24] First described in 1918: White, Walter P., "Calorimetric methods and devices," *J. Am. Chem. Soc.*, **40**, 1897 (1918).

[25] Osborne, N. S., *U. S. Bur. Standards Bull.*, **12**, 28 (1915).

the differential thermels from the jacket wall to a convection shield. The calorimeter is then as free as if no wires were used. The thermal head observations need be only about half as frequent, since the thermal head and the leakage are only half as great in comparison to the main change, $\Delta\Theta$, as with a single gap. In determining the total temperature change the shield must be counted as part of the calorimeter; its temperature variations cancel, however, like those of any other lagging body, if the jacket temperature is either constant or adiabatic.

Increased Uniformity of Temperature. If the temperature over the calorimeter surface is irregular, that over the shield will evidently be much less so. Experiment indicates that for a silver shield 0.1 mm. thick the resulting shield variation will usually be not over 0.2 of the calorimetric. This equalizing effect is added to the action of the distributed junctions to give a very accurate value of the thermal head. If we compare, however, with a calorimeter having a shield with no junctions on it, the gain is only half what this figure would indicate, since such a calorimeter would have a value of K only half as great as the one which must be used with the reading of the shield thermels.

Real Field for the Device. The method has two drawbacks, not mentioned in the original account:

(1) The fastening of thermojunctions, especially insulated ones, to the very thin shield will tend to increase its lag near the points of attachment. (2) The shield will introduce a slight temperature inequality, owing particularly to the greater lag of the parts where vertical and horizontal surfaces join, since these are farther from the calorimeter than the rest. If the calorimeter is highly uniform the shield will be less so. Hence the special field of this device is where exceptionally feeble stirring is desirable or where some other cause of unusual irregularity in calorimeter surface temperature exists.

Chapter VI

Applications to Calorimeter Design and the Planning of Installations

In this section there will be kept in mind the distinction already pointed out between precision as defined in this book, that is, as measured by the largest error probably occurring one time in 300, when experiments are duplicated and averaged, and precision as often measured by the probable error, or error occurring about half the time in single experiments. The first is about three times as severe a test as the other.

The precision of a given calorimeter, as estimated here, may be different from that indicated by practical experience, for two reasons:

(a) In many installations the largest error is in the associated measurements or operations (furnace temperature, purity of chemicals, sampling, see page 25), so that the real excellence of the calorimeter does not appear.

(b) On the other hand, the calorimeter itself, under constant conditions, may show an agreement which is misleading as to its probable performance under all circumstances. Evaporation may vary with the weather, other effects with the time required for the experiment, temperature equalization and stirring heat with the viscosity of the liquid used. The possibility of concealed errors from such causes as these seems evident enough.

All values given will be for the calorimeter of Table IV, unless other dimensions are stated.

Section 25. "Best Commercial" Precision

Precision pretty surely 3 per mille; probable error, 1 per mille.

Each single error should be as small as 0.3 per mille.

A 10″ lag, by **(L2)**, page 87, causes $\frac{10}{60} \times .002\Delta\Theta$ or $0.0003\Delta\Theta$ difference in the result if the thermal leakiness, K, is 0.002. Unless the lag varies by a large part of itself it will cause no appreciable error, even if K is 0.003. Since 10 seconds is a relatively large lag, except

for some thermometers, whose lag ordinarily cancels completely, the question of lag, including stirring lag, need cause no special thought.

Timing follows the same law (Equation 20) as lag, and had best be to 5″ or less.

The effect of change, ε, in an unmeasured jacket temperature, by (15), will be 0.02ε for ten-minute periods, and for this to be $0.0003\Delta\Theta$, ε must be $.015\Delta\Theta$, or not over 0.045° for a rise of 3°. If K for the jacket is 0.0025 the jacket-to-air difference may be 1.8°, but no more with safety. The change in the jacket resulting from heating of the calorimeter is $KT\Delta\Theta$, say $.02\Delta\Theta$, times the ratio of the heat capacities of jacket and calorimeter. For this to be $0.015\Delta\Theta$ the jacket might have about the same capacity! For shorter periods or a smaller K the jacket change may be proportionately greater, and vice versa.

If the stirring heat is 0.001° per minute, the heat in 10 minutes is 0.01°, or 10 times 0.0003 of 3°. Hence such heat needs to be constant to better than 10 per cent, which means a speed constant to 3 per cent. "Constant" here refers only to the change from one ten-minute period to the next, if any of the temperature-loss methods of (6) to (14) is used. Nevertheless, it seems better to have the heat nearer 0.0001° per minute, since the here normally negligible stirring lag error will not be much increased.

For a rise of 3° a probable error in each principal temperature measurement of 0.005° is sufficiently small, and will usually be attainable with good thermometers graduated to 0.01°.

If the temperature loss in the experimental period is taken as simply equal to that in the rating period, which amounts to ignoring $A\tau$ of Figure 5, the error may possibly be $K\tau\Delta\Theta$, or perhaps $0.002\Delta\Theta$, but will usually be much less than that (*see* page 42). Hence this approximation can usually be employed, especially when the calorimeter is calibrated by experiments in which the temperature pattern is about the same as in the other work, but the possibility of employing it will depend on circumstances, and cannot be assumed. It can easily be tested if the X-period thermal head can be measured.

As to convection error, taking the period at 10 minutes, as we have done in this section, the time of rapid rise, T_B, is likely to be around 2 minutes. The convectional part of K (see page 81) is 0.000 066 for a 12 mm. gap and 5°. The allowable value, 0.000 02 for 0.1 per mille precision and 2 minutes, is 0.000 6 for 3 per mille. Hence the convection may approach $\frac{0.000\,6}{0.000\,066}$ or 9 times the value for 12 mm. Table 3 indicates that the gap may therefore safely be 24 mm., which,

by Table 4, makes K less than 0.0012. Such a diminution in K lessens the error from jacket temperature change, which may be troublesome. Moreover the estimate 0.0006 is for a 5° rise and a rather small calorimeter. With a larger calorimeter, and especially with a 3° rise, the convection is appreciably smaller, by an amount which Table 3 leaves uncertain, perhaps 0.4 as much. A gap of 32 mm. or a little more might then be used for the same convection error. The resulting gain in K, however, is now very small indeed, so it seems better to stop at 24 mm. and enjoy either the smaller convection or the possibility of increasing the temperature rise without having the convection become too great.

This convection, however, tho it causes a negligible convection error, is far from imperceptible. With 5° rise and 2 cm. gap it may add 23 per cent to K, making a variation of 0.003 for a 10-minute period. This will very seldom interfere with the use of the Second Geophysical Laboratory Method (Section 2), since only when $\frac{\theta_x - \theta_r}{\Delta\Theta}$ is more than 0.15 will the error from change in K reach the limiting value of 0.0003. But when a predetermined value of K is to be used the possible error, 3 per mille, is quite too large for a single error. It will then be better to add a convection shield if evaporation is made very slight, or to use a Dewar flask to lessen both convection and evaporation. Since the convection shield causes no inconvenience after it is once installed, the practical choice is between the inconveniences of restraining evaporation and adsorption, and those of the glass vessel.

Unrestricted evaporation adds about 0.001 to the thermal leakiness, K, or $0.01\Delta\Theta$ for a ten-minute period. Hence it must not vary effectively more than 3 per cent during an experiment. That amount of variation in straight distillation is unlikely.

The heat corresponding to the process of changing the saturation of the air gap is about 1 per mille of the total if the otherwise advantageous gap of 24 mm. is used, and if the adiabatic method is used. This is too much to allow for a single source of error, but it only counts when the length of period varies. In ordinary working the change of saturation is much less (see page 103), and the vapor which accomplishes it is diverted, so to speak, from the condensation which follows the vaporization. The resulting effect on the initial vaporization rate is uncertain, but small enough to be neglected.

According to the estimates in Section 11, adsorption error is not hard to render negligible for 3 per mille precision in ordinary short experiments. This is almost certainly true for the "nearly tight" closing

of the calorimeter in non-adiabatic working, and probably for the adiabatic open calorimeter. The open non-adiabatic calorimeter must be regarded with less confidence at present, because, while the rate at which adsorption goes on is sufficiently slow to be treated as nearly regular, the re-evaporation rate of the adsorbed water is very likely to be much faster, and is quite unknown. Elaborate discussion is inappropriate, both because the existing data scarcely warrant it, and because we may hope to have much fuller data soon.

On the whole, then, adsorption and jacket-temperature change are the only threatening sources of error, with evaporation the only other one which need cause any uneasiness. Convection also needs attention for work with a predetermined value of K.

The three chief schemes for diminishing thermal leakiness, namely, the adiabatic method, the convection shield, and the Dewar flask, are not only unnecessary here, but are of very little use, since the first two act by lessening convection and so permitting a thick air gap, and here the thick air gap can be used anyway, while the Dewar does not give much less thermal leakiness than the 24-mm. gap. The adiabatic method, however, might well be held in reserve to enable the 24-mm. gap to be used for more accurate work. It introduces no appreciable errors, so that it would be desirable in all cases for those who consider it more convenient than the ordinary method. The Dewar affords the same possibility of passing to greater precision, and also avoids adsorption trouble, by limiting the evaporation to a small space whose walls can be kept thoroughly wet. If such a space is made by means of a sleeve with an ordinary calorimeter, it is safer to have vapor-absorbing material in the outer air gap, so that this procedure is little, if any, better than other means of restricting or preventing evaporation. A sheet copper jacket cover (Section 21) is generally to be recommended with the Dewar. The rubber stoppers often used with it probably do not introduce appreciable error in working to 3 per mille. No discussion of their error appears to have been published by any of those who have used them.

Organic liquid, used instead of water, is not likely to cause any errors serious with 3 per mille precision. Accordingly its advantages may be freely sought. These are, chiefly, a larger temperature rise where a larger heat quantity or a smaller calorimeter with water are not desirable, and a much smaller thermal effect of evaporation in an *uncovered* calorimeter. There may be a question whether the disadvantages of the organic liquid are greater than those of restricting the evaporation of water.

Aneroid calorimeters at ordinary temperatures are easily more than good enough for 3 per mille precision. In a copper block aneroid, since the effective temperature distribution lag is not over 15 seconds for 10 cm. diameter and the variation of it considerably less than that, a mercury thermometer, or any thermometer necessitating a temperature measurement at one point, could be used for this degree of precision. At ordinary temperatures the chief advantage appears to be avoiding the frequent removals of the calorimeter and the weighing of the water. At high and low temperatures the use of fluids is usually undesirable, for various reasons. The jacket temperature with aneroids needs to be either regulated, or more strictly constant than with stirred calorimeters, since the imperfection of temperature equalization can be treated as a lag, which does not cancel unless the jacket temperature is either constant, or equal to the calorimeter. The error from failure of constancy is $LK\varepsilon$, where L is the lag in minutes, K the thermal leakiness, ε the change in jacket temperature during the X-period.

Section 26. "Assured" Precision of 1 per Mille, That Is, 0.3 per Mille Probable Error of One Experiment

This degree of precision is that of most of the best work done hitherto. Each single error should be as small as 0.1 per mille. The requirements can in most instances be readily derived from the estimates of the preceding paragraphs, on 3 per mille precision. It thus follows that: The jacket, to be satisfactorily constant, must not be over 0.6° away from the room in temperature for 10-minute periods, or 2.4° for 5-minute periods, which means that observing or control of the jacket temperature will often be needed.

The time of any lag, multiplied by its variability, must be 3 seconds (or for $K = 0.003$, 4.5 seconds) in order to begin to be appreciable. Thus, even stirring lag, which may reach 10 seconds, will still be negligible unless it varies over 30 per cent. Most lags are therefore still quite negligible with experimental calibration, and even stirring lag will only cause error in exceptional circumstances. The errors then, tho, will be likely to be concealed and systematic; they might come from differences in the viscosity of the liquid, or from large changes in the stirring speed. The last, of course, are preventable. Where the jacket temperature is observed, and therefore may be allowed to vary without detriment to the determination of the temperature loss, η, any variation occurring may cause a lag error. This error will ordinarily be quite negligible (see page 92), but the possibility that it may not be should not be lost sight of.

Timing should be to 3 seconds, and preferably closer.

There is still more reason than before for keeping the stirring heat down to 0.0001° per minute. This, for a 10-minute period, makes a constancy of 10 per cent in speed sufficient, if the temperature rise is 3°. The need of a governor is avoided; the addition of a governor, with faster stirring, would have as its main advantage merely a diminution in the stirring lag, which is usually not important for this degree of precision. With liquids of notably variable viscosity, where a smaller stirring lag might count, there would also be a large variation in the heat of stirring, and a governor is of no use in avoiding error from this source. In general there will be no such error of appreciable amount. For much longer periods, say 2 hours, a governor should easily keep the stirring heat error negligible, but a lessening of the speed to 0.4 would do the same, with a 2.5-fold stirring lag. This last would be proper if the stirring lag were known to be considerably less than 10″ in the first place. As elsewhere in this book, a propeller stirrer in a tube is assumed and no responsibility is taken regarding other kinds.

From the estimate (page 59) of 0.03 scale division as the probable error of a good thermometer reading, the mercury thermometer graduated to 0.01° is just barely good enough for 1 per mille "assured" precision. Its error should be about the largest in the calorimeter, since most of the other single errors can and should each be made smaller than the limiting value, 0.0001 per mille. The errors of electric thermometers should be easily negligible.

Convection must stop at one-third of the value it may have for 3 per mille precision, in order to render negligible the principal convection error of page 80. That is, the convectional part of K should be not over 0.0002 for 5° thermal head. For this head, by Table III, the convection effect increases as the cube of the gap thickness between 8 and 24 mm. Applying this rate of increase, the gap, 12 mm. for 0.0006 convectional K, may be 17 mm., and the total K, accordingly, by Table IV, not over 0.0015.

The lessening of convection as precision increases leaves the second Geophysical Laboratory method still satisfactory. Counting the total convection effect as a variation in K, the maximum error from it up to 5° is 0.0002 $T_x(\theta_x - \theta_r)$, which is negligible, that is, not over 0.0001, as long as $\frac{\theta_x - \theta_r}{\Delta\Theta}$ is not over 0.05, for $T_x = 10$ minutes. The convection shield makes the method much more satisfactory, and is desirable for several reasons if the time much exceeds 10 minutes. As usual,

the Dewar and the adiabatic method are excellent alternatives. Since the possible convection effect, 0.0002, is over 12 per cent of the total K, error from other sources affecting the second Geophysical Laboratory method seems quite negligible ordinarily.

The temperature loss determination method which neglects the difference of φ_r and φ_x, thus avoiding all observations during the temperature rise, is by no means out of the question for this degree of precision, but great care must be exercised to be sure that it is justifiable in any given case.

For work with a predetermined value of K and no rating periods KT_x must be constant to 0.0001, while it is about 10×0.002, or 0.02, for a 10-minute period. This demands K constant to one-half per cent, with corresponding precision in the constant rate, w. Such precision cannot be promised at present. Its assured attainment does not seem impossible, but it would constitute a further development in calorimetry. Aside from other variation, it demands a value of convectional K varying from one experiment to another no more than 0.000 01, if the period is 10 minutes.

Evaporation and adsorption now begin to raise serious questions. The estimates in Section 11 indicate that in non-adiabatic operation the "nearly tight" cover can be used with negligible error from either if each period is not over 20 minutes. With the calorimeter open evaporation needs to be constant to 1 per cent, and the possibilities of adsorption are so dubious that a general condemnation of the non-adiabatic open calorimeter for this degree of precision seems justified. In adiabatic work the open calorimeter is liable to error from incomplete saturation of the air space if the gap is as thick as is otherwise desirable. Section 11 may be consulted for details. As to the adsorption error, the reader is referred to Barry's warning. Neither a recommendation nor an absolute condemnation of the adiabatic open calorimeter seems in order.

Error from heat conducted direct from the room along wires or stirrer rods is easily prevented, but can no longer be neglected. The conditions affecting it are so variable that the special discussion, Section 9, had better be consulted.

There is still no great need of the convection shield or the adiabatic method as a means of higher precision. The stirring lag error is the most serious one which is lessened by these devices, and it is not at all serious in 1 per mille precision. On the other hand, even a moderate reduction of it (see Table IV), accompanied by a putting of convection quite below the horizon, is not to be thrown away, and it is

obtained with no inconvenience by the convection shield (Section 24) when evaporation is well restricted. With the adiabatic method the decision may well depend mainly on whether the experimenter considers that method more or less convenient. The vacuum-walled vessel, where its special disadvantages do not condemn it, affords a slightly greater lessening of stirring lag error and a fair control of evaporation and adsorption.

Joule's twin calorimeters, as the easiest way to use electric thermometers, may deserve favorable consideration as something approaching a labor-saving device in work of 1 per mille precision. They may often greatly lessen the necessity for controlling or observing the jacket temperature, since *change* in this will affect the two calorimeters very nearly alike, even if the *total* effect of the jacket is not quite the same for the two. The two sources of error which, next to those in the temperature measurement, are usually most threatening, namely, stirring lag and evaporation, are not much less with a second calorimeter added, since they are effective largely thru irregularity. Some errors peculiar to the twin method are discussed under it.

Organic liquid would probably often make evaporation error negligible without any special restricting arrangements; and the increase of stirring lag error normal with organic liquid would probably often be admissible. Both these probabilities are increased by the Dewar flask.

Aneroid calorimeters can undoubtedly be made to give 1 per mille precision. The copper block aneroid, however, can hardly be counted on to give it without electric temperature measurement or jacket temperature adjustment, and it is safer to say hardly without both.

Section 27. "Assured" Precision 0.3 per Mille; Average Error 0.1 per Mille

This appears to be the best precision yet reported, at any rate outside of the twin method. Each single error should be as small as 0.03 per mille, or 30 per million. Evidently the associated measurements will usually preclude the attainment of 0.3 per mille in the experiment as a whole, tho even in such cases it may be very advantageous to have the error in the calorimeter itself known to be negligible. Precision of 0.3 per mille, tho naturally more exacting than lower degrees, often involves no single feature which deserves to be called difficult.

The conditions for 0.3 per mille precision are more easily stated than for those which have here preceded, since approximate or doubtful methods may now be eliminated. Thus evaporation and adsorption should be prevented, or else restricted, either by a tight cover, or by a

nearly tight cover with drying material in the air gap, or by confining them to a small space whose walls are wet. The jacket temperature should be regulated or observed so that $\varepsilon K T_x$, the effect of its uncertainty, ε, is as small as $0.000\,03\Delta\Theta$, which for $K = .002$, $T_x = 10$, $\Delta\Theta = 3°$ is readily found to be so that ε is under 0.005°. The lag error from jacket temperature change, usually quite negligible, should be surely so. (See page 92.) Timing should be such that, with ε the timing error, εK is 0.000 03, or ε is 0.015 minute, or about 1 second. The effective variation of all lags also must be equally small.

It follows that a stirring lag of 10 seconds would have to be constant to 10 per cent of itself. Such constancy frequently could not be counted upon. In that case cutting down the lag by faster stirring, using a governor to prevent increase of stirring heat error, tho not to be rejected, is the least efficient road to improvement. The lag preferably should be lessened by using a wide propeller tube (say one-third the diameter of the calorimeter, see page 67) and a simple stirring path, and K should be brought down to 0.0013. The means which are almost necessary to avoid convection, if used at all, will make K as small as this in most cases.

It follows, further, that the temperature rise curve should be located with a precision of 1 second for $K = 0.002$, or of 1.4 second for the better value $K = 0.0013$. There is no difficulty in making the observations with this degree of precision, but it may take some contriving to get two observations, or even one, into the rapid part of the rise. Dickinson's Method (page 57) of observing the time when a predetermined temperature is attained does this perfectly, but that method now requires a high degree of uniformity in the different temperature patterns.

The combination method of page 57 is more likely to be adequate, and it, or very numerous timed observations, will often be needed to show whether Dickinson's method in its simplicity is sufficient or not.

In adiabatic work there is little danger of missing a fairly sudden temperature rise, but there may be some question about matching it with a time precision of 1.4 second. Apparently this has sometimes been done. The possible time error here referred to is different from and largely independent of any lag in the stirring, which may have a considerably larger value as long as its effective variation is no more than 1.4 second.

From the previous calculations given in this section regarding convection, it follows that to make convection error negligible by lessening the air gap would demand a gap as thin as 1 cm., and this will generally

make K over 0.002. Since the considerably lower value for K of 0.0013 is now very desirable, it seems particularly bad practice not to adopt some one of the schemes for attaining that, especially since these also give a much greater lessening of convection than does a 1 cm. gap. The convection shield in particular, once installed, causes practically no error or inconvenience where evaporation is controlled.

The adiabatic method or the Dewar can be used instead wherever their other characteristics seem desirable.

The second Geophysical Laboratory method, with its saving of time, can be used quite satisfactorily if, with KT_x having the frequently attainable value 0.013, the product of $\frac{\varphi_x - \varphi_r}{\Delta\Theta}$ and the percentage variation of K is not over $0.000\,030 \div 0.013$, or 0.0023. Taking K as constant to 2 per cent, the fraction can be as large as 0.11. Moreover, with experimental calibration it is not the value of $\frac{\varphi_x - \varphi_r}{\Delta\Theta}$, but only the variation of that value that must be as small as 0.11. Hence this method can generally be used, but this cannot be taken for granted. (See page 42.)

Electric thermometers with one galvanometer scale division for 0.001° have more than sufficient sensitiveness unless the temperature rise is as small as 1°. The values of the auxiliary coils at the time of the experiment need to be consistent with a precision approaching 30 per million. This requirement makes the work, properly speaking, exacting rather than difficult.

Joule's twin calorimeters, in cases where they are applicable, make the temperature measurement much less exacting. They tend to lessen several errors, to an extent which varies considerably, according to circumstances. (*See* Section 18.)

Of course conduction of heat along wires or rods should not be allowed to cause error. Section 9 may again be referred to.

Unless organic liquid could be trusted to cause no appreciable error even tho allowed to evaporate freely, which is very doubtful, it does not seem, in general, to have any great resultant advantage in work of 0.3 per mille precision.

There is every probability that aneroid calorimeters with proper distribution of the electric thermometers measuring the thermal head, and with proper control of that head, should give 0.3 per mille precision, tho this does not appear to have yet been actually done with copper blocks.

A precision of 0.3 per mille, that is, an average accidental error as small as 0.1 per mille, was twice reached over 15 years ago, and one of these cases was very fully reported.[1] The precision was reached despite the fact that the installation was defective in some respects. The air gap was far too thick, so that convection was very large, and yet K was over 0.003. The stirring lag, however, was apparently as small as 3 seconds. The thermometric sensitiveness was only one-third as good as is readily attainable, but the large temperature rises made up for this defect. Analysis of the results left little doubt that the accidental thermometric error was the chief source of final accidental error. The electric heating used tended to minimize stirring lag- and thermal head measurement-error, so that the precision of the calorimeter alone could not certainly be duplicated under all conditions.

Section 28. Precision 0.1 per Mille; Probable Accidental Error 0.03 per Mille. Each Single Error Should Be as Small as 10 per Million.

The associated measurements will rarely be good enough to justify making any great sacrifice in order to attain this degree of precision completely in the calorimeter alone. But the discussions given in this book of the various sources of error indicate that such precision can often be reached without any particular sacrifice, while it is likely to be desirable to secure corresponding precision in respect to as many single errors as possible, in order to simplify the task of hunting trouble (see pages 113 and 114).

The requirements are easily stated: Evaporation, and convection error, are to be prevented. This involves the use of a convection shield [2] or some other suitable special device and thus will bring with it a value of K as low as 0.0013 unless the calorimeter is unusually small. Timing, including the timing of the temperature rise measurement, or of the adiabatic adjustment, is to be 0.5 second or better, tho one or two errors of 1 second can sometimes be tolerated if no others are as large. The stirring lag variation also is to be as small as 0.5 second. Electric measurements are to be consistent to 10 per million. This means that the temperature rise is to be measured with this degree of precision. This may necessitate knowing one or two large coils to better than that, and is likely to do so with resistance thermometers. The uniformity of jacket temperature and conduction thru the jacket should receive due attention. Aneroid calorimeters can probably be

[1] White, Walter P., *Phys. Rev.*, **31**, 686 (1910).
[2] The convection shield, however, is often not very effective for this extreme precision.

used for 0.1 per mille precision, with care as to temperature distribution as affecting measurement.

The second Geophysical Laboratory method is now likely to be satisfactory only if $\frac{\varphi_x - \varphi_r}{\Delta\Theta}$ is certain to vary no more than 0.04 of itself, and may be considered as one to be used only in exceptional cases. Experimenters trying for a precision hitherto almost unknown are not likely to be insistent on special brevity.

Statements in this chapter regarding adsorption and evaporation antedate the late conclusions on pages 107-108, and should be compared with those before being accepted. In particular, the usefulness of the convection shield is less impaired by a slight evaporation than some statements here might indicate.

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